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The Resistance of Douglas-fir to Sulfite Pulping

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THE RESISTANCE OF DOUGLAS-FIR TO SULFITE PULPING

A thesis submitted by

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INTRODUCTION

The over-all problem of pulping inhibitors is of increasing importance as different species of wood are being utilized by the pulp and paper industry. The present knowledge of pulping inhibitors is almost entirely based on the Swedish study of pinosylvin, found in the heartwood of pine, and related compounds.

Douglas-fir (Pseudotsuga taxifolia), a prevalent species of wood in the Pacific Northwest, is not satisfactorily pulped by the conventional calcium-base sulfite pulping process. It has been shown that the bark and wood of this tree contain dihydroquercetin, a 3-hydroxyflavanone with a phloroglucinol nucleus. Although this compound is structurally related to the previously studied phenolic inhibitors, the pulping characteristics of Douglas-fir exhibit certain anomalies which cannot be explained by our present theory of phenolic inhibitors. Therefore, a study of the role of dihydroquercetin in the sulfite pulping resistance of Douglas-fir might yield information that would aid, not only in the utilization of this species of wood, but also in the utilization of black cherry and certain types of larches which contain related flavanoid-type compounds.

A clarified picture of the nature of the pulping resistance in Douglas-fir might be of immediate commercial value. The difficulty in the pulping of this species has forced certain western sulfite mills to trade nearby Douglas-fir to kraft mills in exchange for the easily pulped

western hemlock. Also, the sulfite mills which are pulping western hemlock sawmill waste are forced to use high concentrations of free sulfur dioxide to handle the Douglas-fir which is usually present in small amounts.

HISTORICAL REVIEW

PREVIOUS STUDIES OF THE SULFITE PULPING OF DOUGLAS-FIR

It has long been known that Douglas-fir is difficult to pulp by a conventional calcium-base sulfite cook and the pulping resistance has been attributed to a number of different factors. The pulping resistance of Douglas-fir has been attributed to the pitchy nature of the wood, the lack of sufficient penetration of the cooking liquor into the chips, a more resistant lignin in Douglas-fir, the precipitation of the base in calcium-base Douglas-fir cooks, and the presence of dihydroquercetin which is structurally related to certain established phenolic inhibitors.

Wells and Rue (1) concluded that Douglas-fir is difficult to pulp on account of the pitchy nature of the wood. They reported yields of 45 to 50%, and bleach requirements of 20 to 25%. The unbleached pulp had fair strength, poor color, and was probably somewhat pitchy.

Beuschlein (2) reported that the pulping resistance of Douglas-fir could not be attributed to resinous material in the wood. He extracted Douglas-fir sawdust with an alcohol-benzene mixture and found that the wood remained difficult to pulp. Pulping studies were conducted with sodium-base liquors with 1.0% combined sulfur dioxide and both 3.0 and 4.0% total sulfur dioxide. With a set of conditions that produced a spruce pulp of 49% yield containing 96% cellulose, the extracted Douglas-fir had a 68% yield which contained only 78% cellulose.

Beuschlein concluded that resins were not responsible for the pulping resistance, but rather that the trouble might be in the lignin: "Douglas-fir has a peculiar cell structure which has been used for the identification of this species. Such cell walls may contain a dense packing of lignin, in which case the surface for a chemical reaction would be less than for a loose or less-packed wall."

The chemical nature of Douglas-fir lignin has been studied by two different investigators and their results are in disagreement. Bailey (3) made a study of the lignosulfonic acids from Douglas-fir and concluded that the lignin consists of four trimeric coniferyl aldehyde units, while spruce lignin is composed of three. Brookbank and Brauns (4) made a series of lignin preparations from both Douglas-fir and spruce, and compared both the lignin products and their chemical derivatives. He concluded that there was practically no difference between the lignins in the two species.

The penetration of cooking liquor into Douglas-fir chips has been studied by Chidester and McGovern (5) and Pew (6). Both reports concluded that, although penetration of the cooking liquor into Douglas-fir is somewhat more difficult than penetration into spruce or western hemlock, the wood can be completely penetrated by slightly extending the penetration period of the cooking cycle. Chidester and McGovern also found that Douglas-fir sapwood is more easily penetrated than the heartwood.

Brookbank (7) noted the formation of a precipitate in the cooking liquor near the end of a calcium-base Douglas-fir sulfite cook. Although the precipitate was described as a mixture of calcium sulfate and calcium sulfite, no analytical results were presented. He suggested that Douglas-fir might not increase the monosulfite precipitation temperature of the liquor as does spruce. It was suggested that the calcium sulfate resulted from a bisulfite decomposition due to the presence of pinene-type compounds in the wood. Brookbank concluded: "The problem in the pulping of Douglas-fir heartwood is the precipitation of the cooking liquor and the resultant burning of the pulp."

The liquor precipitation has also been reported by other investigators. Chidester and McGovern (8) noted that "the liquor turns black before the digestion is completed, precipitation often occurs, and the pulp is burned." Hatch and Holzer (9) stated: "Using a calcium-base acid, the base precipitates suddenly toward the end of the cook, making it necessary to blow the charge quickly to prevent burning." The chemical composition of the precipitate was not reported.

The liquor precipitate is not formed when Douglas-fir is pulped with soluble-base sulfite liquors. Chidester and McGovern (8) stated that Douglas-fir is reduced fairly completely by either sodium- or ammonium-base liquors. Pulping is much more difficult with calcium-base liquors, while magnesium falls between these extremes. These conclusions might be somewhat misleading because the total cooking time

was longer with the soluble-base cooks used in these comparisons. They concluded: "The respectively improved pulping with calcium-, magnesium-, and sodium- (or ammonium-) base sulfite cooking liquors would seem to point out that the respective solubilities and stabilities of the cooking reagents and of the products of the cooking reaction play an important part in the pulping of Douglas-fir."

If the liquor precipitation were the result of exceeding the monosulfite precipitation temperature, it might have been eliminated in the experiments of McGovern and Chidester (10). Gishler and Maass (11), in their studies of the monosulfite precipitation temperatures of calcium oxide-water-sulfur dioxide systems, found that small amounts of surface-active agents tend to increase the precipitation temperatures. McGovern and Chidester (10) tested several different wetting agents and found that they had practically no effect on the calcium-base sulfite pulping of Douglas-fir.

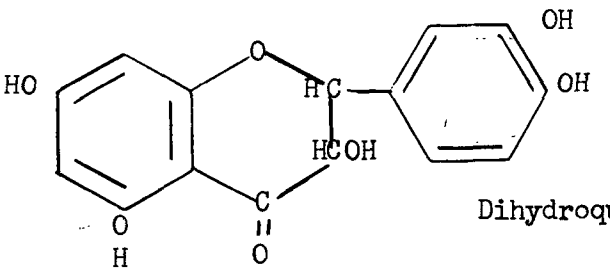
Several different authors have found that the pulping resistance of Douglas-fir seems to be concentrated in the heartwood. Although the sapwood is more difficult to pulp than easily pulped woods such as spruce and western hemlock, it is far superior to the heartwood.

Douglas-fir heartwood can be pulped under certain conditions. Benson (12) patented a scheme for the pre-extraction of the Douglas-fir chips with hot aqueous ammonia to remove resins, coloring matter

and other nonvolatile compounds. The extracted chips, cooked by the sulfite process, yielded a high quality, easily bleached pulp. Other authors have reported that certain ammonia pretreatments allow the successful sulfite pulping of pine heartwood (13, 14).

Douglas-fir can be successfully pulped by calcium-base sulfite liquors if high concentrations of total sulfur dioxide (7 to 8%) are used (5, 7, 15). Brookbank (7) and Chidester and McGovern (5) reported that the pulping could also be improved by reducing the maximum cooking temperature and extending the length of the cook. These authors reduced the maximum temperatures without changing the maximum pressure; therefore, a reduction in temperature was accompanied by an increased sulfur dioxide concentration in the digester.

The first indication that a phenolic inhibitor might be present in Douglas-fir came from the work of Pew (6), who isolated a compound from Douglas-fir heartwood and identified it as 2,3-dihydroquercetin. This compound has also been referred to as Douglas-fir flavanone and taxifolin.

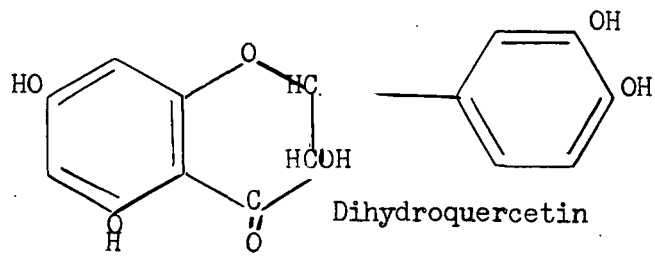


Dihydroquercetin

Pew determined the dihydroquercetin content of several different samples of Douglas-fir heartwood and reported an average concentration of about 1% of the wood, although some samples contained over 2% of the compound. He made a series of spruce cooks, in the presence of a number of pulping inhibitors, and found that dihydroquercetin is a stronger inhibitor than catechol, but weaker than catechin, resorcinol, or phloroglucinol.

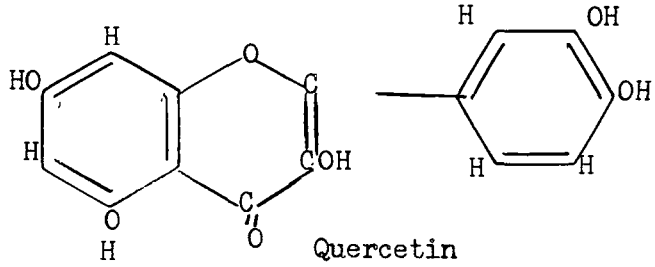
Pew extended his pulping studies to Douglas-fir chips from a second-growth tree. He found that the pulping resistance of Douglas-fir could be somewhat reduced, but never eliminated by preliminary extraction of the chips with alcohol, reduction of the chips size, or vacuum impregnation of the cooking liquor into the chips before cooking. This led to the conclusion that, although dihydroquercetin contributes to the pulping resistance of Douglas-fir, other factors are also involved.

Information concerning the behavior of dihydroquercetin in sulfite cooking liquor was obtained by Kurth and Chan (15a) and Sen (16). Sen found that dihydroquercetin is oxidized to quercetin in sodium-base sulfite cooking liquors at 135°C. The reaction does not occur in water alone. The reduction product was not identified, but after comparing Sen's findings with other oxidations in sulfite cooking liquor, it seemed probable that the bisulfite is reduced to thiosulfate. The probable presence of thiosulfate in Douglas-fir sulfite cooks suggests that the precipitate formation might be the result of thiosulfate-catalyzed bisulfite decomposition.



Dihydroquercetin

Sulfite
Cooking
Liquor



Quercetin

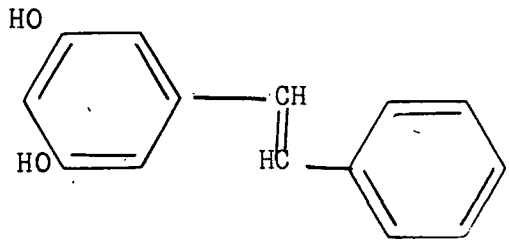
The reaction of dihydroquercetin in sodium bisulfite solutions was described in another report which was presented while this program was in progress. Kurth (17) formed quercetin by refluxing solutions of bisulfite and dihydroquercetin for varying periods of time. The formation of quercetin was also observed with calcium-base acid sulfite liquors, but in this case there was formed on the sides of the flask an inorganic scale which contained quercetin. This caused Kurth to suggest that the difficulty in the calcium-base sulfite pulping of Douglas-fir might be due to the formation of a calcium-quercetin complex. No analytical data were presented to substantiate this suggestion.

A study of the sulfite pulping of Japanese larch (Larix leptolepis) was reported in a Japanese article by Migita and coworkers (18) which appeared during the progress of this work. This species of wood is of particular interest because the authors reported that it contains dihydroquercetin, the compound also present in Douglas-fir. These authors summarized their results with three conclusions:

1. A yield of 65% quercetin was obtained in a cook of isolated dihydroquercetin.
2. The dihydroquercetin-lignin condensation does not occur to any great extent when the compound is cooked in the presence of isolated native lignin.
3. The yellow color of the pulp seems to be due to quercetin, but the quercetin content of the pulp is less than 0.12%.

THE THEORY OF PHENOLIC INHIBITORS

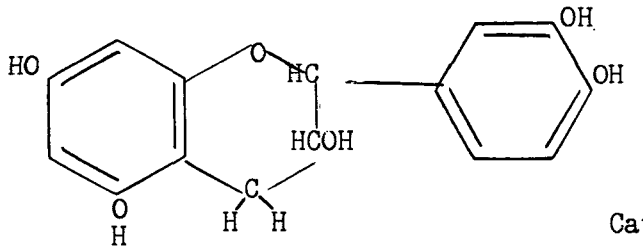
One of the first major contributions to the field of sulfite pulping inhibitors was made by Erdtman (19), who identified the inhibiting compounds in pine heartwood. He isolated pinosylvin and its methyl ethers,



Pinosylvin

and showed that these compounds were directly responsible for the resistance of pine heartwood to sulfite pulping. At the same time, Erdtman showed that polyphenols, in general, are inhibitors. Phenol, itself, has little effect, but compounds such as resorcinol (1,3-dihydroxybenzene) and phloroglucinol (1,3,5-trihydroxybenzene), with hydroxyl groups in a 1,3 configuration are strong inhibitors. Compounds such as catechol, (1,2-dihydroxybenzene), with hydroxyls in a 1,2 configuration have milder effects.

Both Erdtman (20) and Pew (6) have shown that catechin acts as a pulping inhibitor. Catechin, a compound often associated with tannins, is very closely related structurally to the dihydroquercetin in Douglas-fir—the only difference being the presence of a carbonyl group in the 4-position of the latter compound. Catechin is not as strong an inhibitor as resorcinol or phloroglucinol, but is more effective than catechol.



Catechin

The most logical explanation of the mechanism of pulping resistance is the Erdtman "phenolization" theory (19-22), which states that the phenolic compounds condense with the lignin in the wood to form an

insoluble, phenolized lignin product. The phenolic inhibitors react with the lignin groups which normally are sulfonated and thereby prevent satisfactory sulfonation of the lignin.

According to Erdtman, the sulfonation of lignin in a sulfite cook takes place in two distinct stages and there are two different portions of the lignin, groups A and B, which are sulfonated. Group A, that portion of the lignin which is sulfonated first: (1) is sulfonated easily with bisulfite solutions at a pH of 1.5 to 2 and pH values over 3.5, (2) reacts more quickly with phenols than with bisulfite at a pH of 1.5 to 2, (3) reacts more quickly with bisulfite than with phenols at pH values over 3.5. The satisfactory sulfonation of lignin group A is the key to the successful sulfite pulping of woods containing strong phenolic inhibitors.

After the first sulfonation step the lignin is still insoluble. Group B: (1) is sulfonated easily with bisulfite solutions at a pH of 1.5 to 2, (2) does not react at all, or very slowly, with bisulfite solutions at pH values over 3.5, (3) reacts more quickly with bisulfite than with phenols at a pH of 1.5 to 2, (4) does not react at all or very slowly, with phenols at pH values over 3.5. Phenolic inhibitors have little or no effect on this portion of the pulping process.

The detrimental effect of phenolic inhibitors is the result of these compounds entering into a condensation with the lignin to form large complexes. The groups normally sulfonated are involved in the condensation, resulting in a low-sulfonated, insoluble lignin product. After

phenolization has occurred, "only sugar and easily hydrolyzable polysaccharides are removed during the cooking process, leaving cellulose and phenol lignin undissolved" (19).

In agreement with the phenolization theory, it has been shown that pine heartwood (23,24), as well as sprucewood with added phloroglucinol or resorcinol (21), can be pulped by a two-stage sulfite cook. Solutions of sodium bisulfite or sodium monosulfite are used for the first sulfonation step and the cook is then completed with the customary acid cooking liquor.

Phenolization can be minimized in several different ways. Slow rates of temperature rise in the early portion of the cooking cycle are beneficial since sulfonation is favored over phenolization at low temperatures (21). Increased penetration times and vacuum impregnation with the cooking liquor also decrease the effectiveness of inhibition. However, these treatments never completely eliminate the inhibiting effect, as has been shown by Adler and Stockman (25), who used a 96-hour penetration period.

There were several reasons for believing that the sulfite pulping resistance of Douglas-fir could not be explained by the theory of phenolic inhibitors. Chidester and McGovern (8) reported that the successful pulping of Douglas-fir can be accomplished with soluble-base cooking liquors. Soluble-base cooking liquors tend to slightly improve the pulping characteristics of most pulpwoods, but they cannot be successfully used for wood which contains strong phenolic inhibitors.

Douglas-fir also differs from pulpwoods which contain strong phenolic inhibitors in its reaction to formaldehyde. Erdtman (20) has suggested that the lignin-inhibitor condensation is similar to the phenol-formaldehyde condensation. Adler and Stockman (25) seem to have verified this by showing that pine heartwood and spruce containing catechin-type tannins can be successfully pulped by the sulfite process after a pretreatment with formaldehyde solution. The formaldehyde supposedly blocks the active hydrogens on the phenolic inhibitors and thereby prevents them from reacting with the lignin. The formaldehyde reduced the pine heartwood screenings from 19.2 to 1.1%, and the "inhibited" spruce screenings from 36.5 to 2.7%. In contrast, the pulping of Douglas-fir heartwood was not improved by this treatment. This would seem to indicate that the phenolic constituents in Douglas-fir are quite unreactive in a phenol-formaldehyde type of condensation, or that phenolic compounds of this type are not responsible for the pulping resistance of Douglas-fir.

Finally, the formation of a precipitate in the cooking liquor is difficult to explain by the phenolization theory. If this precipitate is connected with the pulping resistance of Douglas-fir it would seem that the pulping resistance is, at least in part, due to some other cause.

BISULFITE DECOMPOSITION REACTIONS

The first detailed study of the decomposition of sulfite solutions was made by Foerster and coworkers (26) in a report published in 1923.

Foerster showed that thiosulfate is a catalyst in the reaction which is expressed by the following over-all equation:

$$4\ HSO_3^- \longrightarrow 2\ SO_4^= + S_2O_3^= + 2\ H^+ + H_2O$$

The stability of thiosulfate depends on the hydrogen-ion concentration according to the equilibrium:

$$HSO_3^- + S^o \rightleftharpoons S_2O_3^= + H^+$$

If the solution becomes sufficiently acidic the over-all reaction becomes:

$$3\ HSO_3^- \longrightarrow 2\ SO_4^= + H^+ + S^o + H_2O$$

Foerster's proposed equations for the various intermediate steps in the over-all bisulfite decomposition are:

$$5\ S_2O_3^= + 6\ H^+ \longrightarrow 2\ S_5O_6^= + 3\ H_2O$$
$$S_5O_6^= + HSO_3^- \longrightarrow S_4O_6^= + S_2O_3^= + H^+$$
$$S_4O_6^= + HSO_3^- \longrightarrow S_3O_6^= + S_2O_3^= + H^+$$
$$S_3O_6^= + H_2O \longrightarrow SO_4^= + S_2O_3^= + 2\ H^+$$

If serious bisulfite decomposition exists in a calcium-base sulfite cook, the formation of sulfate eventually causes the base to precipitate as calcium sulfate. In the case of soluble-base liquors the precipitate is not formed.

Foerster found that concentrated solutions are much more stable than dilute solutions. Also, the more acidic the solutions, the slower

the reactions proceed. When 2 N hydrochloric acid is used as a solvent, the decomposition is completely repressed. High hydrogen-ion concentrations decrease the concentration of bisulfite and prevent the buildup of thiosulfate.

Any compound which causes the formation of thiosulfate in sulfite cooking liquor is a potential cause of bisulfite decomposition. Free sulfur is a well-known promoter of bisulfite decomposition (26-28), presumably through its reaction with bisulfite to form thiosulfate. A number of wood compounds have been shown to react in sulfite liquor to lose hydrogen atoms and reduce bisulfite to thiosulfate. The generally accepted equation for this reaction is as follows:

$$4\,[H] + 2\,HSO_3^- \longrightarrow S_2O_3^{=} + 3\,H_2O$$

This reaction takes place in the presence of terpenes (29), free sugars (30-32), and formic acid (33). Prior to this program the effect of dihydroquercetin on sulfite cooking liquor had not been determined, although it was known that the compound was dehydrogenated to form quercetin.

PRESENTATION OF THE PROBLEM

The published descriptions of the pulping characteristics of Douglas-fir refer to certain phenomena which cannot be explained by the well-known theory of phenolic inhibitors. These include the formation of a precipitate in the cooking liquor and the strong dependence of the pulping characteristics on the cooking liquor base. It is known that Douglas-fir contains dihydroquercetin, a compound which is structurally related to proven phenolic inhibitors. However, the dihydroquercetin is different from known phenolic inhibitors in that it is oxidized to quercetin by the sulfite cooking liquor. These facts suggested that a study of the pulping resistance of Douglas-fir might yield new information concerning the mechanism of pulping resistance.

The objectives of this program were five-fold:

1. To learn whether the sulfite pulping resistance of Douglas-fir can be adequately explained by the presence of dihydroquercetin.
2. To learn whether Douglas-fir and dihydroquercetin behave according to the theory of phenolic inhibitors.
3. To learn what significant effects the oxidation of dihydroquercetin to quercetin might have on the sulfite pulping characteristics of Douglas-fir.
4. To learn the nature, the cause, and the significance of the precipitate which forms in conventional calcium-base sulfite cooks of Douglas-fir.
5. To gain clearer insight into the dependence of the sulfite pulping of Douglas-fir on the type of base in the cooking liquor.

EXPERIMENTAL PROCEDURES

SPECIAL METHODS

ANALYSIS OF DISSOLVED MIXTURES OF SULFITE, THIOSULFATE, AND POLYTHIONATES

Theory of the Analysis

One of the chief difficulties in analyzing the various components of partially decomposed, acidic sulfite liquors is the necessity of neutralizing the solution in order to carry out certain steps in the analysis. In neutral solutions, the polythionates are decomposed through their reactions with sulfite and a strong element of uncertainty is introduced into the results of conventional methods. Special techniques to minimize the difficulties accompanying neutralization have been proposed, but, in general, they are either inaccurate or difficult to evaluate (34). These factors forced the development of a new set of analytical procedures which measured the changes taking place with neutralization and used this information to calculate the components in the original acidic system. This method of analysis embodies the sulfite conversion of trithionate and the sulfite-blocking procedures proposed by Kurtenacker (34).

The analytical procedure required the assumption that trithionate is absent in the acidic sulfite liquor. Kurtenacker (34) stated that trithionate rapidly decomposes in an acidic medium such as 1 N hydrochloric acid. Samuelson and Westlin (35) reported that trithionate is very unstable in an acidic medium and it is improbable that it should

be present in sulfite spent liquor. Stam, Seipold, and Goehring (36) have found that trithionate quickly decomposes in the presence of sulfurous acid if the temperatures exceed 40°C. It has also been shown that trithionate is stable in cool, neutral sulfite solutions (34,35).

Solutions containing sulfite and polythionates undergo chemical changes when they are neutralized. For the purpose of explanation, consider an acidic solution containing a mixture of sulfite, thiosulfate and tetrathionate ions. Upon neutralization, the following reaction takes place quantitatively, providing an excess of sulfite is present:

$$S_4O_6^{=} + SO_3^{=} \longrightarrow S_3O_6^{=} + S_2O_3^{=}$$

One mole of trithionate is formed for each mole of tetrathionate in the original solution. Since no trithionate was present in the original acidic solution, the resultant trithionate in the neutral solution is a measure of the tetrathionate originally present and also a measure of the amount of thiosulfate formed from the tetrathionate. With this information, it is possible to calculate the amount of sulfite, thiosulfate, and tetrathionate in the acidic solution by analyzing for sulfite, thiosulfate, and trithionate in the neutral solution.

Reactions in the Analysis

The reactions in the three-step analytical procedure are as follows. Consider an acidic solution containing X moles of sulfite ion, Y moles

of thiosulfate ion, and Z moles of tetrathionate ion. Upon neutralization, the reaction takes place to form a mixture of (X - Z) moles of sulfite ion, (Y + Z) moles of thiosulfate ion, and Z moles of trithionate ion. The iodine consumptions of sulfite, thiosulfate, and trithionate are two, one, and zero equivalents per mole, respectively. The number of equivalents of iodine (A) consumed by the mixture is

$$2\,(X - Z) + (Y + Z) = 2X + Y - Z = (A).$$

The second step of the procedure measures the number of equivalents of iodine (B) consumed by the thiosulfate alone. This is accomplished by direct titration of the neutralized solution after blocking the sulfite with formaldehyde.

$$Y + Z = (B)$$

The third step measures the amount of trithionate present. The neutralized mixture is first titrated with iodine to the starch endpoint.

$$(X - Z)\quad [SO_3^{=} + 2\,I^{\circ} + H_2O \longrightarrow SO_4^{=} + 2\,HI]$$

$$(Y + Z)\quad [S_2O_3^{=} + I^{\circ} \longrightarrow 1/2\,S_4O_6^{=} + I^{-}]$$

$$Z\,S_3O_6^{=} + I^{\circ} \longrightarrow \text{No reaction}$$

Neglecting the sulfate, which does not enter into the succeeding reactions, the oxidized solution contains a mixture of 1/2(Y + Z) moles

of tetrathonate ion and Z moles of trithionate ion. This is then treated with an excess of sulfide. The trithionate enters into the well-known reaction:

$$Z\ S_3O_6^{=} + Z\ S^{=} \longrightarrow 2Z\ S_2O_3^{=}$$

The tetrathionate also reacts with sulfide but the reaction details are not known. Separate tests showed that the reaction products have an iodine consumption of two equivalents for each mole of tetrathionate originally present. The excess sulfide is removed and the number of equivalents of iodine consumption (C) is equal to Y + 3Z.

In summary, the procedure requires the three iodine titrations on the neutral solution to obtain the numerical values of (A), (B), and (C). The values of X, Y, and Z, which represent the composition of the acidic solution are determined from the simultaneous equations. The assumption was made that all the trithionate present in the neutral solution was formed from the reaction between polythionates and neutral sulfite, and no trithionate was present in the acidic solution. The complete details of the analytical procedure are presented in Appendix B.

Accuracy of the Analysis

This analytical procedure was tested on a series of solutions of known composition. The various components were mixed in a neutral solution and allowed to stand for several minutes prior to the analysis. The reactions which took place within the mixtures prior to the analyses

should have been similar to those which occur in neutralized sulfite cooking liquor. The known mixtures were prepared from standardized solutions of c.p. reagents, except tetrathionate which was prepared by the iodine oxidation of thiosulfate.

The results are presented in Table I. Each figure in the table represents one titration. Tables I and II include all the analyses which were conducted on solutions of known composition. The calculated analytical results are in satisfactory agreement with the known compositions of the mixtures.

Analysis of Mixtures Containing Free Sulfur and/or Higher Polythionates

The outlined analytical procedure does not give an accurate picture of the amount of free sulfur or higher polythionates present in the original acidic solution. However, these other components are effectively determined as equivalent sulfite, thiosulfate, and tetrathionate. In this way, the analytical procedure remains an effective and practical measure of the degradation of acidic sulfite solutions.

The higher polythionates react with cool, neutral sulfite in a series of consecutive reactions which eventually form trithionate (34).

$$S_6O_6^{=} + SO_3^{=} \longrightarrow S_5O_6^{=} + S_2O_3^{=}$$
$$S_5O_6^{=} + SO_3^{=} \longrightarrow S_4O_6^{=} + S_2O_3^{=}$$
$$S_4O_6^{=} + SO_3^{=} \longrightarrow S_3O_6^{=} + S_2O_3^{=}$$
$$S_3O_6^{=} + SO_3^{=} \longrightarrow \text{No reaction}$$

TABLE I

ANALYSIS OF MIXTURES OF SULFITE, THIOSULFATE, AND TETRATHIONATE

Run	Constituent	Added Quantity [a]	Value Determined by Analysis [a]
85A	Sulfite	9.88	9.70
	Thiosulfate	1.52	1.56
	Tetrathionate	0.76	0.72
87C	Sulfite	9.83	9.79
	Thiosulfate	1.01	1.09
	Tetrathionate	1.52	1.47
87D	Sulfite	9.83	10.14
	Thiosulfate	0.00	0.02
	Tetrathionate	1.52	1.59
88E	Sulfite	9.83	9.82
	Thiosulfate	2.02	2.00
	Tetrathionate	0.00	0.01
88F	Sulfite	4.91	4.84
	Thiosulfate	2.52	2.55
	Tetrathionate	1.26	1.25
89G	Sulfite	9.83	9.78
	Thiosulfate	0.51	0.48
	Tetrathionate	0.51	0.54
90H	Sulfite	9.75	9.63
	Thiosulfate	1.01	1.02
	Tetrathionate	1.01	1.01
92K	Sulfite	1.95	1.91
	Thiosulfate	1.01	1.04
	Tetrathionate	1.01	0.99

[a] All values are expressed as millimoles of constituent in the original 200 ml. sample.

Since all polythionates are calculated as tetrathionate, the presence of "n" moles of polythionate existing as $S_5O_6^=$ causes the analytical results to be "n" moles lower for sulfite and "n" moles higher for thiosulfate. Hexathionate would cause a "2n" mole change in the results. The calculated number of moles of tetrathionate will be correct for polythionate regardless of the form in which it exits.

Free sulfur might react with a neutral mixture of sulfite and polythionate in either of two ways, but in either case, the net effect on the analysis is the same. The most obvious reaction is the direct combination with sulfite.

$$S^o + SO_3^= \longrightarrow S_2O_3^=$$

The second method is by reaction with a polythionate which, in turn, reacts with sulfite.

$$S_4O_6^= + S^o \longrightarrow S_5O_6^=$$

$$S_5O_6^= + SO_3^= \longrightarrow S_4O_6^= + S_2O_3^=$$

By either of these methods, "n" moles of free sulfur consume "n" moles of sulfite and form "n" moles of thiosulfate.

Several trial analyses of known solutions were used to confirm this effect. Free colloidal sulfur was prepared by the iodine oxidation of a standardized sulfide solution and different amounts of this suspension were added to a sulfite-thiosulfate-tetrathionate

mixture. Prior to the analysis, the solution was allowed to stand for several minutes, after which the colloidal sulfur was completely dissolved. These results are presented in Table II.

TABLE II

THE EFFECT OF COLLOIDAL SULFUR

Run	Constituent	Added Quantity [a]	Value Determined by Analysis [a]
90H	Sulfite	9.75	9.63
	Thiosulfate	1.01	1.02
	Tetrathionate	1.01	1.01
	Free sulfur	0.00	--
90I	Sulfite	9.75	9.47
	Thiosulfate	1.01	1.26
	Tetrathionate	1.01	1.01
	Free sulfur	0.25	--
91J	Sulfite	9.75	9.20
	Thiosulfate	1.01	1.52
	Tetrathionate	1.01	0.99
	Free sulfur	0.50	--

[a] All values are expressed as millimoles of constituent in the original 200 ml. sample.

In conclusion, the outlined method of analysis can be used if two conditions exist:

1. The original solution must be sufficiently acidic or sufficiently hot to decompose trithionate.
2. The solution must contain sufficient sulfite to allow the following reaction to take place after the solution has been neutralized.

$$S_nO_6^{=} + (n-3)\,SO_3^{=} \longrightarrow (n-3)\,S_2O_3^{=} + S_3O_6^{=}$$

The outlined analytical procedure gives a satisfactory picture of the sulfite-thiosulfate-tetrathionate relationship in sulfite cooking liquor. In the presence of free sulfur or higher polythionates, the calculated results correspond to conditions which exist after these compounds have reacted with sulfite to form thiosulfate and tetrathionate. Although the results do not give a true picture of the specific polythionates in the mixture, the calculated results give an accurate estimate of the extent of cooking liquor degradation.

DETERMINATION OF DISSOLVED SULFATE IN THE PRESENCE OF SULFITE, THIOSULFATE AND POLYTHIONATES

The method for determining sulfate in the presence of sulfite, thiosulfate, and polythionates was patterned very closely after the method proposed by Kurtenacker (34). The sulfate was determined gravimetrically after precipitation with barium chloride. The sulfite was blocked by the addition of formaldehyde and the thiosulfate was oxidized to tetrathionate. Tetrathionate does not affect the barium sulfate precipitation if it is conducted in dilute solutions at room temperature.

The method was tested on a number of solutions in which the sulfate ion represented a small fraction of the sulfur-bearing ions present. The known solutions were prepared by mixing solutions of the sodium salts of the various compounds. Calcium chloride was added to each mixture to obtain a calcium-sulfur ratio similar to that found in

sulfite cooking liquor. In each case, sulfate analyses were run on the sulfite solutions used in preparing the known mixtures, and these results were then used to correct the known amounts of sulfate added. The results of all the analyses which were used to test this analytical procedure are shown in Table III.

The analytical results in Table III show that the determination is accurate to within a few per cent, and the results tend to be somewhat higher than the true values. The detailed analytical procedure is presented in Appendix B.

ANALYSIS OF SOLID MIXTURES OF CALCIUM SULFATE, CALCIUM SULFITE, AND FREE SULFUR

A method of analysis was developed for determining the composition of precipitates which were formed in calcium-base sulfite cooks of Douglas-fir.

This procedure was limited to determinations of sulfate, sulfite, and free sulfur. Calcium thiosulfate would not be found in these precipitates because of its high solubility and its instability at temperatures over 80°C. (37). The acidity of the system prevents the precipitation of solid calcium sulfide. Polythionic acids are liquids which do not exist in the water-free state, and therefore, would not be found in the precipitates. Salts of the polythionic acids would not be present since they are stable only in dry air in the absence of other sulfur-containing compounds.

TABLE III

SULFATE ANALYSIS

Run	Millimoles of Constituent Added			Excess $BaCl_2$ Added, %[a]	Millimoles of Sulfate from Analysis	Percent[b] Error
	Sulfate	Sulfite	Thiosulfate			
48-5	0.611	10	2	23	0.599	- 2.4
48-6	0.611	10	2	105	0.623	+ 2.0
48-7	0.611	10	2	392	0.628	+ 2.8
48-8	0.611	10	2	1,540	0.628	+ 2.8
51-6	0.603	10	2	108	0.624	+ 3.5
51-7	0.603	10	2	108	0.619	+ 2.7
51-8	1.106	10	4	58	1.121	+ 1.3
51-9	1.106	10	4	58	1.121	+ 1.3
54-3	1.108	10	8	80	1.131	+ 2.1
54-4	1.108	10	8	80	1.120	+ 1.2
54-5	1.303	5	5	47	1.317	+ 1.1
54-6	1.303	5	5	47	1.309	+ 0.4
54-7	0.610	10	10	228	0.643	+ 5.4
54-8	0.610	10	10	228	0.631	+ 3.3
54-9	0.610	10	0	228	0.631	+ 3.3

[a] Based on the theoretical amount of $BaCl_2$ required to precipitate the sulfate.

[b] Based on the amount of sulfate added to the known solution.

The scheme of precipitate analysis measures the amounts of sulfite, sulfate, and free sulfur, and assumes that the solid sulfite and sulfate are present as the calcium salts. The first step in the analysis is the determination of sulfite by the direct iodine oxidation of a water suspension of the precipitate.

$$CaSO_3 + I_2 + H_2O \longrightarrow CaSO_4 + 2\ HI$$

The resulting suspension is a mixture of calcium sulfate and free sulfur. This is acidified with hydrochloric acid to dissolve the calcium sulfate and the insoluble free sulfur is removed by filtration. The sum of the sulfite and sulfate in the original sample is obtained from the gravimetric determination of sulfate as barium sulfate. The free sulfur is determined by dissolving it in a boiling solution of sodium sulfite to form thiosulfate, blocking the excess sulfite with formaldehyde, and titrating the thiosulfate with iodine solution. These reactions are as follows:

$$S^o + Na_2SO_3 \longrightarrow Na_2S_2O_3$$

$$2\ S_2O_3^{=} + I_2 \longrightarrow S_4O_6^{=} + 2\ I^-$$

The method of analysis was tested on several known mixtures of calcium sulfite, calcium sulfate, and free sulfur. The calcium sulfate and free sulfur were added as accurately weighed small amounts of the solid reagents. The calcium sulfite was added as a slurry prepared from sodium sulfite and an 8% excess of calcium chloride. Tests showed that

about 98% of the sulfite was present in the solid phase of the slurry. The amount of sulfate in the known mixtures was corrected for the very low sulfate concentration of the sulfite slurry, determined by separate analysis. Table IV lists all the analyses of known mixtures which were conducted with this analytical procedure. Each figure in the table is the result of a single determination. The detailed analytical procedure is presented in Appendix C.

THE PREPARATION OF DIHYDROQUERCETIN

Extraction and Purification

The dihydroquercetin used in this program was extracted from the cork layers which are present in Douglas-fir bark. The dihydroquercetin is much more concentrated in the bark than in the heartwood— Pew (6) obtained maximum yields of 2.2% from the heartwood, while Hergert and Kurth (38) obtained up to 23% from the cork layers of the inner bark.

The bark was obtained from the Weyerhaeuser Timber Co., of Longview, Washington. In ordering the bark, it was requested that it be from old, mature trees. The bark had been removed from the log by the hydraulic barker, and to reduce shipping weight, most of the dry, black, outer bark had been removed.

The wet bark was first reduced by passing it through a chipper. The remaining size-reduction steps were conducted in a Rietz mill—an adaptation of a hammermill, with a vertical axis. The starting material, after chipping, was 60 pounds of wet bark of undetermined moisture

TABLE IV

ANALYSIS OF SOLID MIXTURES

Run	Constituent	Added Quantity [a]	Value Determined by Analysis [a]
115D	Calcium sulfate	1.18	1.15
	Calcium sulfite	0.00	--
	Free sulfur	3.39	3.34
120A	Calcium sulfate	1.09	1.05
	Calcium sulfite	0.95	0.94
	Free sulfur	5.11	--[b]
120B	Calcium sulfate	2.17	2.06
	Calcium sulfite	0.95	0.96
	Free sulfur	4.11	4.01
120C	Calcium sulfate	2.14	2.03
	Calcium sulfite	0.95	0.92
	Free sulfur	0.66	0.66
120D	Calcium sulfate	2.46	2.36
	Calcium sulfite	0.95	0.95
	Free sulfur	4.66	4.48
120E	Calcium sulfate	2.39	2.29
	Calcium sulfite	0.95	0.94
	Free sulfur	13.32	12.87
120F	Calcium sulfate	1.19	1.13
	Calcium sulfite	0.95	0.93
	Free sulfur	2.56	2.51

[a] All values are expressed in millimoles of constituent.

[b] Discontinued due to omission of step in analysis.

content. The bark was subjected to four passes through the Rietz mill and the minus-20 mesh fraction was discarded after each step. The final plus-20 mesh fraction, weighing 4 pounds, was a cork product of fairly high purity. However, undetermined amounts of bast fibers were still present.

The cork product was reduced further by a single pass through a Wiley mill, using a bedplate with 0.08-inch holes. The plus-60 mesh fraction was used for extraction.

The cork product was pre-extracted with benzene, air dried, and then extracted with ether. The crude ether extract was dried at 60°C. in a vacuum oven. The yield of crude extract from the 4 pounds of cork product was 102 grams. The extract was given three successive recrystallizations and treatments with Darco decolorizing carbon, using 7.5 liters of hot water in the first step and 6 liters in each of the latter two steps. The final yield of dihydroquercetin, dried several hours at 105°C., was 33.1 grams. Two additional, smaller batches of dihydroquercetin were prepared with similar procedures.

The crude ether extract contained 20 to 30% of a hot water-insoluble, heat-sensitive material. A portion of this material was dissolved in ethanol at 50°C., and upon cooling, the material reprecipitated. The precipitate was a creamy, yellow-tan, amorphous material which turned brown upon exposure to air. The filtrate was a deep, reddish brown. The chemical nature of this precipitate and the filtrate were not determined.

Proof of Identity and Purity

Five different dihydroquercetin products were compared on the basis of melting point, optical activity, and chromatography. These were the three batches of dihydroquercetin prepared for this program, a commercial sample purchased from the Krishell Laboratories, of Portland, Oregon, and an authentic sample from Pew at the Forest Products Laboratories, who first isolated and identified this compound from the heartwood of Douglas-fir. The first four samples had been extracted from Douglas-fir bark, while the latter had been isolated from the heartwood.

TABLE V

MELTING POINTS OF DIHYDROQUERCETIN SAMPLES

Origin of Product	Melting Point, °C.
Pew	241 - 2 (dec.)
Krishell	240 - 1 (dec.)
Hoge batch 1	241 - 2 (dec.)
Hoge batch 2	242 - 3 (dec.)
Hoge batch 3	242 - 3 (dec.)
Pew + Hoge batch 1	241 - 2 (dec.)

The melting point of dihydroquercetin is dependent on the rate of heating. In the determinations listed above, the temperature was quickly raised to about 235°, and then slowly to the melting point. Melting points below 225° were obtained with the same products using very slow rates of heating.

TABLE VI

OPTICAL ROTATIONS OF THE DIHYDROQUERCETIN SAMPLES
(1:1, Acetone-Water Solvent)

Origin of Product	Optical Rotation, $[\alpha]_D^{25}$
Pew	+ 46° (c,4) (6) [a]
Krishell	+ 47° (c,3-1/2)
Hoge batch 1	+ 44° (c,4)
Hoge batch 2	+ 45° (c,4)
Hoge batch 3	+ 45° (c,4)

a Measured at 20°C.

The dihydroquercetin products were compared chromatographically, using 0.01 N hydrochloric acid as the developer and a freshly prepared mixture of 1% solutions of ferric chloride and potassium ferricyanide as the spray reagent. All products gave a strong mark of dihydroquercetin at an R_f* of about 0.27 to 0.30. The four bark products showed very faint spots at an R_f of about 0.08. The Pew product, from Douglas-fir heartwood, had a slight impurity which was not moved by the developer. This impurity could have been quercetin.

None of the samples studied were 100% dihydroquercetin. However, due to the favorable comparisons of the melting points and the optical rotations, along with the chromatographic indication that the impurities were very slight, it was concluded that any of these products were of sufficient purity for use in this thesis program.

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* The R_f factor is the ratio of the distance moved by the compound to the distance moved by the total solvent front.

THE CHROMATOGRAPHY OF PHENOLIC COMPOUNDS

The use of paper partition chromatography for the resolution of individual components of organic mixtures is well established. The primary requirement of a chromatographic system, for use in this program, was the ability to make a clean separation of dihydroquercetin and quercetin. There was no published description of a system that had been shown to meet this requirement.

Several developers (irrigating solvents) successfully used with various other types of organic compounds were tested and found to be unsatisfactory. These were: 10 (parts by volume) butanol, 3 pyridine, 3 water; 9 ethyl acetate, 2 acetic acid, 2 water; water-saturated butanol; and butanol saturated with 2% aqueous ammonia.

The first successful separation of dihydroquercetin and quercetin was obtained with a developer of carbon dioxide saturated water, proposed by Barton, Evans, and Gardner (39). These authors had worked with dihydroquercetin, but not with quercetin. It was found that dihydroquercetin had an R_f of 0.25 to 0.45, depending on the chromatograph temperature, the gas-phase concentration of carbon dioxide during the developing, and the age of the developer solution. The quercetin was not moved by the carbonic acid developer.

Additional experiments were conducted in the search for a developer that would be more stable and less sensitive to its environment. Distilled water acted much like the carbonic acid solution and made a

complete separation of the two compounds. Quercetin remained on the starting point with an R_f of 0, but the dihydroquercetin formed a long streak between the R_f values of 0.3 and 0.6. The next developer tested was a solvent of 0.01 N hydrochloric acid. Quercetin was not moved and the dihydroquercetin was concentrated into short streaks at an R_f of 0.28. This developer was adopted for all the chromatographic work.

Barton and coworkers (39) proposed a freshly prepared spray reagent of equal volumes of 1% solutions of ferric chloride and potassium ferricyanide. The phenolic compounds then appeared as dark blue spots on the paper. In order to fix the chromatogram and prevent the background from becoming blue upon standing, the freshly sprayed paper is successively washed in a dilute hydrochloric acid solution (1 N hydrochloric acid is satisfactory) and water. Barton's method was found to be satisfactory and was used in all the chromatographic work.

All of the chromatograms prepared by this method had a line, which seemed to be a solvent front, across the paper at an R_f value of about 0.7. This line, which becomes visible after spraying, was studied by streaking the chromatograms, still wet with the developer, with indicator solutions of methyl red and thymol blue. The line was found to be the zone of a sharp pH gradient. It was shown that, with a 0.01 N hydrochloric acid developer, the water moves faster than the hydrochloric acid and the faint line at an R_f of about 0.7, which appears after spraying, is the location of an acid front.

In the course of the experimental work, five different phenolic compounds were studied with the described developer and spray reagent: quercetin (R_f = 0), dihydroquercetin (R_f = 0.28), catechin (R_f = 0.39), phloroglucinol (R_f = 0.51), and resorcinol (R_f = 0.66). All chromatograms were made with Whatman No. 1 filter paper with the solvent front moving downward. The paper was removed from the developer bath after the solvent front had moved about 18 inches. This usually took about 4 hours.

PULPING PROCEDURES

DESCRIPTION OF EQUIPMENT

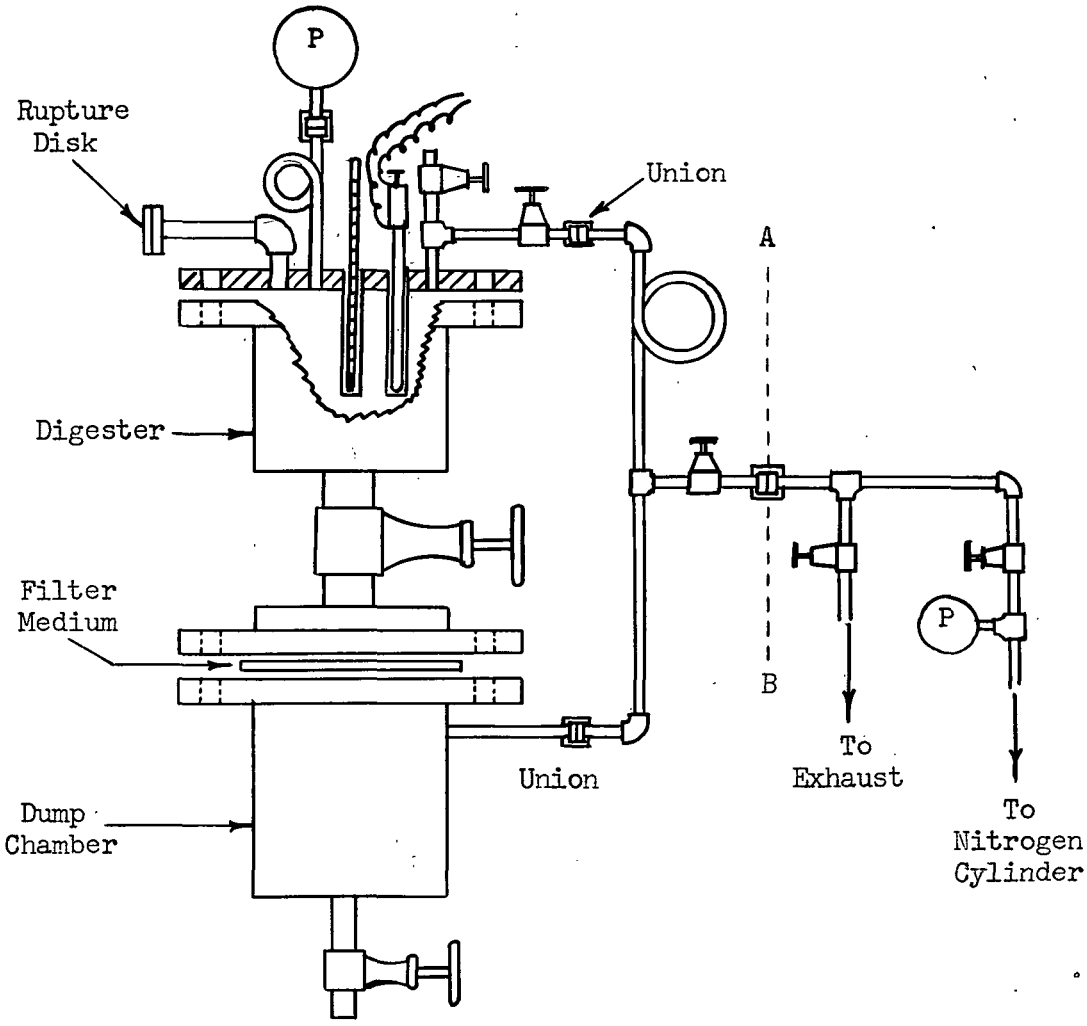
The One-Liter Digester

All the sulfite cooks conducted in the absence of wood, plus a portion of the cooks with wood, were carried out in a small digester built specially for this program. The usuable volume of the digester was about one liter. A schematic diagram of the one-liter digester is shown in Figure 1.

The combined digester and dump chamber were mounted on a vertical stand equipped for shaking. Pillow blocks were used to mount the bottom of the shaker stand to a fixed shaft which was the axis of the shaking motion. All the piping to the right of the line AB (see Fig. 1) was permanently fixed to a rigid support. To shake the apparatus it was necessary to open the pipe union (shown on the line AB), slide the stand away from the permanent piping and connect the shaker drive.

Figure 1

The One-Liter Digester



Equipment to the left of line AB is mounted on the shaker rack.

The shaking was obtained by moving the top part of the stand back and forth with a crankshaft and connecting rod. The shaking frequency was 47 revolutions per minute and the amplitude at the reaction chamber was 3-1/2 inches.

The digester and the dump chamber were built from lengths of 4-inch diameter, schedule 40, 316 stainless steel pipe. The bottoms were out from 304 stainless steel quarter-inch plate and they were welded to the pipe. The flanges were carbon steel, positioned to prevent contact with the cooking liquor. The digester lid was cut from half-inch, 316 stainless steel plate.

The digester, along with the adjacent piping that could not be disconnected, had a volume of approximately 1150 ml. The reaction chamber had the following attachments through the lid: a pressure gage, a rupture disk assembly, an entrance line for adding the cooking liquor or relieving the digester, and two thermometer wells. The second thermometer well was used to insert a mercury-bulb temperature regulator.

The digester was heated with a six-foot length of serpentine heating coil with a rated capacity of 5 watts per lineal inch. This heating coil was wound around the outer periphery of the unprotected pipe. The combined pipe and heating coil were covered with a thick layer of asbestos insulation. The rate of heating was controlled manually by a 0 to 130-volt powerstat with a rated capacity of 8 amperes. With this heating arrangement, it was possible to reach 140°C. in about 90 minutes at 115 volts.

The dump chamber was equipped for rapid cooling with a copper cooling coil wound around its outer surface. By circulating tap water at about 10°C., through this coil, it was possible to cool the liquor from 140°C. to below room temperature in 10 minutes.

The 38-Liter Digester

Several sulfite cooks of spruce and Douglas-fir were conducted in the Institute pulping laboratory digester number one. This is a vertical, stationary, flat-bottomed, stainless steel digester with a total volume of 38 liters. The digester had a liquor recirculation rate of 24 liters per minute and all cooks were made with indirect steam heating. A sample line, from the liquor recirculation line, allowed convenient liquor sampling during the progress of the cook.

WOOD PROCUREMENT AND PREPARATION

Several seasoned and barked spruce logs, about 6 inches in diameter were obtained from the woodlot of a nearby sulfite pulp mill. Chips, averaging one-half inch in the fiber direction, were prepared in a 4-knife, 36-inch Carthage chipper. The chips were screened on a 4-mesh screen to remove the undersized debris. The chips were then carefully inspected and the knots and oversized particles were removed manually. The finished chips were analyzed for moisture content, bagged, and stored at 8°C. prior to use.

The Douglas-fir used in these experiments was obtained from two different sources. Sample A was a pie-shaped cut of a 107-year-old tree obtained from the Crown Zellerbach Corporation, of Camas, Washington.

The diameter of the barked log was 32 inches and it contained 82% heartwood, on a volume basis. Sample A was used only in the preliminary work investigating the chemical composition of the precipitate formed in the calcium-base sulfite pulping of Douglas-fir.

The Douglas-fir sample B, which was used in all the other pulping studies, was a representative sample of a log cross section obtained from the Weyerhaeuser Timber Company, of Longview, Washington. This tree was 275 years old, with a diameter of 29 inches, excluding the bark. This sample contained 90% heartwood, on a volume basis.

The chip preparation and storing of the Douglas-fir samples were the same as those used for the sprucewood.

PREPARATION OF THE COOKING LIQUOR

The required weight of calcium oxide, calcium hydroxide or sodium hydroxide of c.p. purity, was added to the proper amount of cold water to yield the desired concentration of combined sulfur dioxide in the final liquor. Sulfur dioxide gas, of refrigerant quality, was bubbled into the slurry until a very slight excess had been added—the progress of the sulfur dioxide addition was followed by the weight increase. The solution was then cooled, if necessary, to approximately 20°C. The total sulfur dioxide content was determined by iodine titration and the proper amount of water and base were added to obtain a cooking liquor of the desired composition. The liquor was then stored overnight in a tightly stoppered, almost completely filled bottle. Fresh

cooking liquor was prepared for each cook. The cooking liquor for use in the one-liter digester was prepared with distilled water. The liquor for use in the 38-liter digester was prepared with city water.

OBTAINING EXPRESSED LIQUOR SAMPLES

Samples of the cooking liquor which was present in the interiors of the chips were desired in certain of the pulping studies. After the cooks were completed, the liquor was drained off and the chips were allowed to drain for an additional 15 minutes before the digester was opened. The chips were quickly removed from the digester and immediately masticated in a small Banbury mixer. The pulp was then transferred to a Buchner funnel containing a sheet of filter paper. A rubber sheet diaphragm was placed over the top of the funnel and a vacuum was applied to the filter flask. After sufficient liquor for analysis had been pressed from the pulp, the vacuum was turned off and the pulp was saved for other analyses.

The expressed liquor was analyzed immediately after it had been removed from the pulp. If the expressed liquor from a calcium-base cook was allowed to stand, a precipitate, which was presumably calcium sulfate, often settled out.

Expressed liquor samples obtained in this manner cannot be used to make comparisons with the drained liquor because the vacuum in the filter flask probably causes a major loss of free sulfur dioxide. However, differences between the relationship between the expressed and drained liquors in different sulfite cooks can probably be safely

used to detect any serious blocking of the chip pores that might prevent diffusion of cooking liquor into the chips or reaction products out of the chips. For accurate comparison of the expressed and drained liquors in a single cook, the liquor should be removed from the pulp under conditions that would prevent the loss of sulfur dioxide.

THE IMPREGNATION PROCEDURE

Several sulfite cooks were made with spruce chips impregnated with dihydroquercetin. The impregnation procedure was as follows. The chips were evacuated for 30 minutes, a warm aqueous solution of dihydroquercetin was added, nitrogen gas was admitted and a pressure of 100 p.s.i. was held for 30 minutes. The pressure was then slowly relieved, over a 15-minute period, and the excess solution was drained off. The chips were air dried to about 10% moisture prior to pulping.

The amount of dihydroquercetin added to the chips was calculated from the difference in total solids between the original and final solutions, corrected for the amount of water-extractable material removed from the wood in separate tests, using water alone.

This treatment did not give a uniform distribution of dihydroquercetin throughout the chips. Ferric chloride stain reactions on dried chip cross sections showed that, although dihydroquercetin was present in the centers of the chips, the concentration was not as great as that near the chip ends.

ANALYSIS OF SULFITE SPENT LIQUOR

Combined Sulfur Dioxide

The combined sulfur dioxide concentration in sulfite spent liquors was determined by the Sander method (40). This method consists of two successive alkali titrations to the methyl orange endpoint. The first titration neutralizes the free sulfurous acid to the bisulfite. Then, an excess of mercuric chloride is added, which forms a complex with the bisulfite and liberates an equivalent amount of hydrochloric acid. The second alkali titration to the methyl orange endpoint is a measure of the total sulfur dioxide. The combined sulfur dioxide concentration is determined from the difference between the two titrations. Since the methyl orange endpoint is difficult to detect in deeply colored liquor samples, all titrations in this work were carried to a pH of 3.5.

Under certain conditions, negative values of combined sulfur dioxide are obtained from this procedure. This occurs when the base has been completely consumed and free sulfuric acid is present. The sulfuric acid increases the alkali consumption in the first titration and has no effect on the second titration. Therefore, a negative value of combined sulfur dioxide could result.

Free Sulfur Dioxide

The free sulfur dioxide concentrations in sulfite spent liquors were determined by direct iodine titration according to Institute Method 111.

Thiosulfate

The thiosulfate concentrations in the sulfite spent liquors were determined by the method of Samuelson and Westlin (35). This method is based on the formation of the alpha-oxysulfonic acid through the combination of the sulfite and formaldehyde. The alpha-oxysulfonic acid is not affected by the iodine and the thiosulfate can be titrated directly without the influence of the sulfite. These authors have shown that the errors are usually less than 3% of the resultant answer and the analysis results tend to be lower than the calculated results from known samples.

Sulfate

The sulfate concentrations in sulfite spent liquor samples were determined by the procedure described earlier for the analysis of dissolved sulfate in the present of sulfite, thiosulfate, and polythonates. In this method, the diluted solution from the thiosulfate analysis is treated with an excess of 0.1 N barium chloride. This procedure is similar to the method used by Sillen (41), except the method of Sillen does not include the oxidation of thiosulfate to tetrathionate prior to the barium chloride treatment. Sillen's sulfate method has been criticized since the results tend to be one to three per cent too high (42). Kurtenacker (34) has shown that results from the sulfate analysis tend to be too high in the presence of unoxidized thiosulfate.

PULP ANALYSES

Permanganate Number

The permanganate numbers of pulps were determined by Institute Method 410. For permanganate numbers over 35, 5.00 milliequivalents of permanganate and 50 ml. of 4 N sulfuric acid were added to one gram of pulp in a total volume of 1500 ml.

Alcohol Solubility

The alcohol solubility of pulp was determined by extracting air-dried samples for four hours in a Soxhlet extractor with 95% ethanol. The final alcohol solution was filtered, evaporated to near dryness and dried for two hours at 60°C. in the vacuum oven.

Screenings

Screenings were determined as that portion of the total yield which would not pass through a flat screen with 0.010-inch slots.

Insoluble Lignin

The insoluble lignin in pulp was determined by the standard 72% sulfuric acid method, described in Institute Method 428. The strong acid treatment hydrolyzes the polysaccharide portion of the pulp and the remaining insoluble material is considered to be lignin. This residue is then filtered, washed, and determined gravimetrically.

Soluble Lignin

The soluble lignin in pulp can be defined as lignin which is dissolved by the standard 72% sulfuric acid method. It has been generally known that the 72% sulfuric acid method is inadequate in the determination of the total amount of lignin-type material in pulp (43). The failure of all the lignin to appear as acid-insoluble material seems to be very serious in pulps with low lignin contents. The increased acid solubility of the lignin in wood pulp might be due to a partial solubilization in the pulping process. The soluble lignin determination is a method for estimating the amount of lignin in the pulp which failed to appear as insoluble material in the 72% sulfuric acid method.

At the present time there is no exact method for determining the soluble lignin. The most commonly used procedure involves the estimation of the soluble lignin by the ultraviolet absorbance* measurements on the combined filtrate and washings from the 72% sulfuric acid lignin determination. The concentration of soluble lignin is calculated from the absorbance of the solution and the known absorptivity of purified lignin, usually spruce native lignin. In most cases these calculations have been conducted at a wavelength of 280 millimicrons, where the ultraviolet absorptivity curve of spruce native lignin exhibits a maximum.

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* The terminology recommended by the joint committee on nomenclature is used in this paper. Anal. Chem. 24:1349(1952).

The soluble lignin procedure is handicapped by two potential major sources of error. First, there might be differences between the absorptivity curves of the soluble lignin and the purified native lignin which is used as a standard. Also, a number of nonligneous sugar derivatives such as furfural and hydroxymethylfurfural, formed by the treatment of wood polysaccharides with sulfuric acid, tend to have high ultraviolet absorptivities at about 280 millimicrons where the soluble lignin is usually determined (43-45).

The soluble lignin values in this program were calculated from the absorbance of the lignin filtrates at four different wavelengths—230, 250, 280, and 300 millimicrons. The calculated soluble lignin concentration at these different wavelengths are presented in Appendix A. The calculations were based on the absorptivity curve of spruce native lignin which was reported by Barton (46). The absorptivities of spruce native lignin at these wavelengths are 46.5, 18.0, 18.0, and 8.2 respectively. In each case, the minimum value of soluble lignin was that which was calculated at 230 millimicrons. At this wavelength the possible error introduced by carbohydrates is minimized due to the high absorptivity of the lignin and the low absorptivity of the sugar products. Therefore, all values of soluble lignin which appear in the experimental results were calculated at a wavelength of 230 millimicrons, based on the absorptivity curve of spruce native lignin. All measurements were made with a Beckman Model DU spectrophotometer. The cell thickness was 1 cm. The lignin filtrates, from one-gram samples, were diluted to one liter prior to the measurements.

In summary, the reported values of soluble lignin must be considered as approximations of the true value. In effect, the soluble lignin is an estimated correction factor for the error which is known to exist in the standard lignin determination by the sulfuric acid method. The potential errors in the determination of soluble lignin could be quite large, but these errors are probably less important than the errors which would exist without this correction.

Total Sulfur in Pulp

The total sulfur in the pulp was determined by a sodium peroxide oxidation in a small bomb, followed by the conventional total sulfur analysis described in Institute Method 109.

EXPERIMENTAL RESULTS

STUDY OF THE PRECIPITATE FORMED IN DOUGLAS-FIR COOKS

Several different authors (5, 7, 8, 9) have reported the formation of a precipitate in calcium-base sulfite cooks of Douglas-fir. However, there were no records of an investigation of its chemical composition. Three calcium-base sulfite cooks of Douglas-fir Sample A (107 years old) were conducted to obtain precipitate samples. These cooks are described in Table VII.

The light tan precipitate, which had the appearance of a fine beach sand, seemed to be evenly distributed throughout the digester charge. The recovery of this material from these cooks was not complete. The precipitate was separated from the fibers by mixing the pulp with water, allowing the mixture to stand for several minutes, and collecting the precipitate from the bottom of the container. The precipitates were quickly placed in weighing bottles and dried at 80°C. in a nitrogen atmosphere. The dried samples were ground in a mortar and weighed prior to the chemical analyses.

The data of Table VII show that the precipitates from the Douglas-fir cooks were primarily anhydrous calcium sulfate. In each cook, the precipitate contained about 90% sulfate, calculated as calcium sulfate. The amount of free sulfur in the precipitates was small, but its presence was verified by sulfur crystals which were formed on the sides of the weighing bottle during the drying of the precipitate from Cook 3.

TABLE VII

PRECIPITATES FROM DOUGLAS-FIR COOKS

Temperature cycle: 1 hour to 90°, 1/2 hour from 90 to 100°, 1 hour from 100 to 110°, 2 hours from 110 to 120°, 4 hours from 120 to 145°, remainder at 145°C.
Maximum pressure: 85 p.s.i. Pressure was relieved to 50 p.s.i. during the last 15 minutes prior to the blow.
Digester: One-liter

	Cook 1	Cook 2	Cook 3
Wood	Whole wood	Whole wood	Heartwood
Liquor composition			
Combined SO_2, %	1.20	1.25	1.25
Total SO_2, %	6.75	6.14	6.10
Liquor ratio	8:1	7-1/2:1	6-1/2:1
Total time of cooking, hr.	10-1/2	10-1/2	12
Screened yield, % [a]	48.3	49.8	35.1
Screenings, % [b]	3.7	1.2	21.8
Permanganate number (screened pulp)	17.8	19.6	Over 35
G.E. Brightness, %	25.2	20.5	14.2
Precipitate analysis			
Grams of precipitate recovered	2.06	1.16	2.40
Sulfate, as $CaSO_4$, %	90.0	91.7	89.4
Sulfite, as $CaSO_3$, %	0.9	1.0	0.8
Free sulfur, %	0.4	0.8	2.1
Loss on combustion, %	5.8	3.7	4.2

[a] Based on the ovendry wood
[b] Based on the unscreened pulp

The predominance of calcium sulfate in the precipitate, along with the definite presence of small amounts of free sulfur, is a strong indication that it was caused by thiosulfate-catalyzed bisulfite decomposition. The very small fraction of calcium sulfite indicates that the precipitate was not the result of exceeding the monosulfite precipitation temperature of the cooking liquor.

THE DECOMPOSITION OF SULFITE COOKING LIQUOR

INTRODUCTION

The decomposition of sulfite cooking liquor in the presence of thiosulfate and dihydroquercetin was studied by obtaining the curves for decomposition vs. time. The catalytic effects of these compounds were then compared with those of phloroglucinol, resorcinol, catechin, formic acid, free sugars, and free sulfur by comparing the degrees of decomposition after ten hours at 140°C. A series of cooks were also conducted to determine the effect of temperature on the rate of bisulfite decomposition.

All cooks were conducted in the absence of wood, with sodium-base cooking liquors carefully standardized to 6.00 $\pm$ 0.03% total sulfur dioxide and 1.40% combined sulfur dioxide. Sodium-base liquors were used after preliminary tests showed that the desired temperatures could not be attained with calcim-base liquors without exceeding the monosulfite precipitation temperature. The thiosulfate and the formic acid were added to the liquor as the sodium salts. In these cases, the

original base content was reduced to allow for the sodium in these additives. The sulfur content of the original liquor was correspondingly reduced when thiosulfate and free sulfur were added. In all cases, the liquor had a sulfur concentration of 938 milliatoms per liter and a sodium concentration of 437 milliatoms per liter.

All cooks were conducted in the one-liter digester. The lid was secured on the empty digester and the air was swept out with a stream of nitrogen gas. The liquor charge (900 ml.) was then added through the entrance line after opening the gage line to allow the escape of the excess nitrogen from the digester. The digester was tightly closed and the cooks were conducted without pressure relief. In each case, the liquor was heated from 20° to 140° in about 95 minutes and maintained at constant 140°C. for the remainder of the cook.

All analyses of the decomposed solutions were carried out in duplicate. If the results from the two analyses were in poor agreement, additional analyses were conducted.

THIOSULFATE-CATALYZED DECOMPOSITION

The effect of thiosulfate on the bisulfite decomposition in sulfite cooking liquor was studied for several reasons. Some compounds catalyze bisulfite decomposition by reacting with the cooking liquor to form thiosulfate, which, according to Foerster (26), is the true catalyst in these reactions. The direct addition of thiosulfate allowed an insight into the nature of the decomposition under these

experimental conditions, without the possible side effects which might accompany bisulfite decomposition catalyzed by other additives. Also, these experiments were designed to obtain kinetic data which were later used to compare other decomposition catalysts.

Thiosulfate-catalyzed liquor decomposition was studied in a series of cooks in which the only variable was the time of reaction. In each cook, 7.0 millimoles per liter of thiosulfate had been added to the original liquor. This is equivalent to the theoretical amount of thiosulfate that could be formed in a sulfite cook of Douglas-fir containing 2.1% dihydroquercetin, with a liquor ratio of 5 to 1. The summary of the data obtained from these cooks is presented in Table VIII.

TABLE VIII

THIOSULFATE-CATALYZED BISULFITE DECOMPOSITION

Cooking liquor: Sodium base, 1.40% combined SO_2, 6.00% total SO_2
Thiosulfate added: 6.97 millimoles per liter

Time	Decomposition Products Millimoles per Liter			Percent of Sulfur in Decomposition Products [a]
	Sulfate	Thiosulfate	Polythionate	
Before heating	2.7	7.4	0.4	2.0
After heating to 140°	5.0	6.0	1.5	2.5
3 hours at 140°	14.2	10.8	1.0	4.2
6 hours at 140°	34.9	19.1	2.9	9.0
8 hours at 140°	57.2	30.5	2.2	13.6
10 hours at 140°	105	47.7	5.7	23.8

[a] These figures include the thiosulfate added to the original liquor.

The data of Table VIII agree with the descriptions of bisulfite decomposition reported by Foerster (26). The molar ratio of sulfate to thiosulfate approximates 2:1. The polythionate concentration is a measure of the amount of sulfur present in the intermediate reactions of the over-all decomposition. The reasons for the apparently erratic polythionate data are not known.

The semilogarithmic plot of the sulfate and thiosulfate concentrations *vs.* time are shown in Figure 2. The straight-line relationships indicate that the data agree with the equation for a first-order reaction:

$$\ln c = kt + C$$

Where c is the concentration
k is the specific reaction rate
t is the time
C is a constant

The specific reaction rate, k, calculated from the thiosulfate increase, is 0.21 hours^{-1}. The compliance with the equation for a first-order reaction shows that the rate of thiosulfate increase is proportional to the thiosulfate concentration.

DIHYDROQUERCETIN-CATALYZED DECOMPOSITION

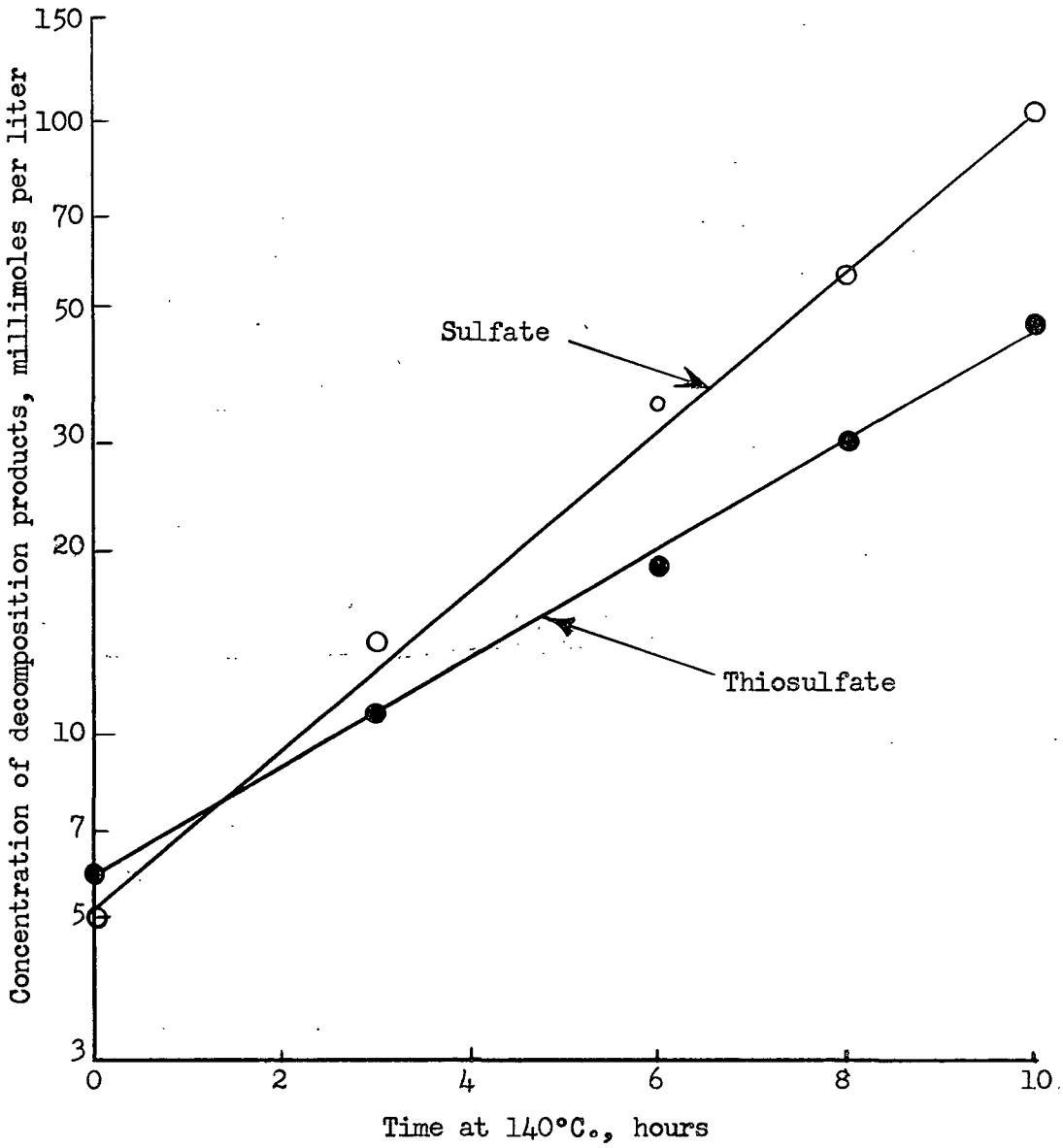
Four sulfite cooks, in the absence of wood, were conducted with liquors containing dihydroquercetin. The dihydroquercetin was added to the digester in dry, crystalline form prior to securing the cover. The compound was presumably dissolved in the liquor, with the help of agitation, during the early part of the temperature rise. The

Figure 2

Concentration vs. Time
(Semilogarithmic Plot)

Thiosulfate-Catalyzed Decomposition of

Sodium-Base Sulfite Cooking Liquor



concentration used in this study was slightly over four grams per liter. Complete solution of the dihydroquercetin was probably obtained because Sen (16) found that 20 grams per liter of dihydroquercetin were readily dissolved in sodium-base sulfite liquor at 100°C.

The concentration of dihydroquercetin used in these experiments was approximately 14.0 millimoles per liter. This corresponds to a 2.1% concentration in the wood, using a liquor ratio of 5:1. This is exactly twice the molar concentration used in the preceding experiments with thiosulfate. The molar concentration was doubled because it was expected that two moles of dihydroquercetin are required to form one mole of thiosulfate in the liquor. The data from these cooks are presented in Table IX.

TABLE IX

THE EFFECT OF DIHYDROQUERCETIN ON SULFITE COOKING LIQUOR STABILITY

Cooking liquor: Sodium base, 1.40% combined SO_2 6.00% total SO_2
Dihydroquercetin added: 13.94 millimoles per liter

Hours at 140°	Decomposition Products Millimoles per Liter			Sulfur in Decomposition Products, %	Per Cent Yield of Quercetin
	Sulfate	Thiosulfate	Polythionate		
3.75	11.3	6.7	0.0	2.6	46.6
7	23.8	12.6	0.2	5.3	44.5
10	50.3	22.5	2.3	11.1	45.7
12	88.5	40.3	3.7	19.6	50.0

When the logarithms of the sulfate and thiosulfate concentrations are plotted against time, the points fall on a straight line, but the data are more erratic than in the previous series of cooks with thiosulfate. These data are shown in the curves of Figure 3. Judging from the semi-log plots, the 12-hour thiosulfate concentration seems to be the most erratic point. This point seems to be about 5 millimoles, or over 10% too high. A part of this deviation might be attributed to the high degree of dihydroquercetin oxidation in this cook, shown by the high quercetin yield.

The specific reaction rate, $\underline{k}$, calculated from the rate of thiosulfate increase in dihydroquercetin-catalyzed decompositions is 0.20 hours^{-1}. This is approximately the same value of $\underline{k}$ calculated from the cooks in which thiosulfate was directly added. The close agreement between the calculated specific reaction rates suggests that the mechanism of the bisulfite decomposition is the same in thiosulfate- and dihydroquercetin-catalyzed cooks.

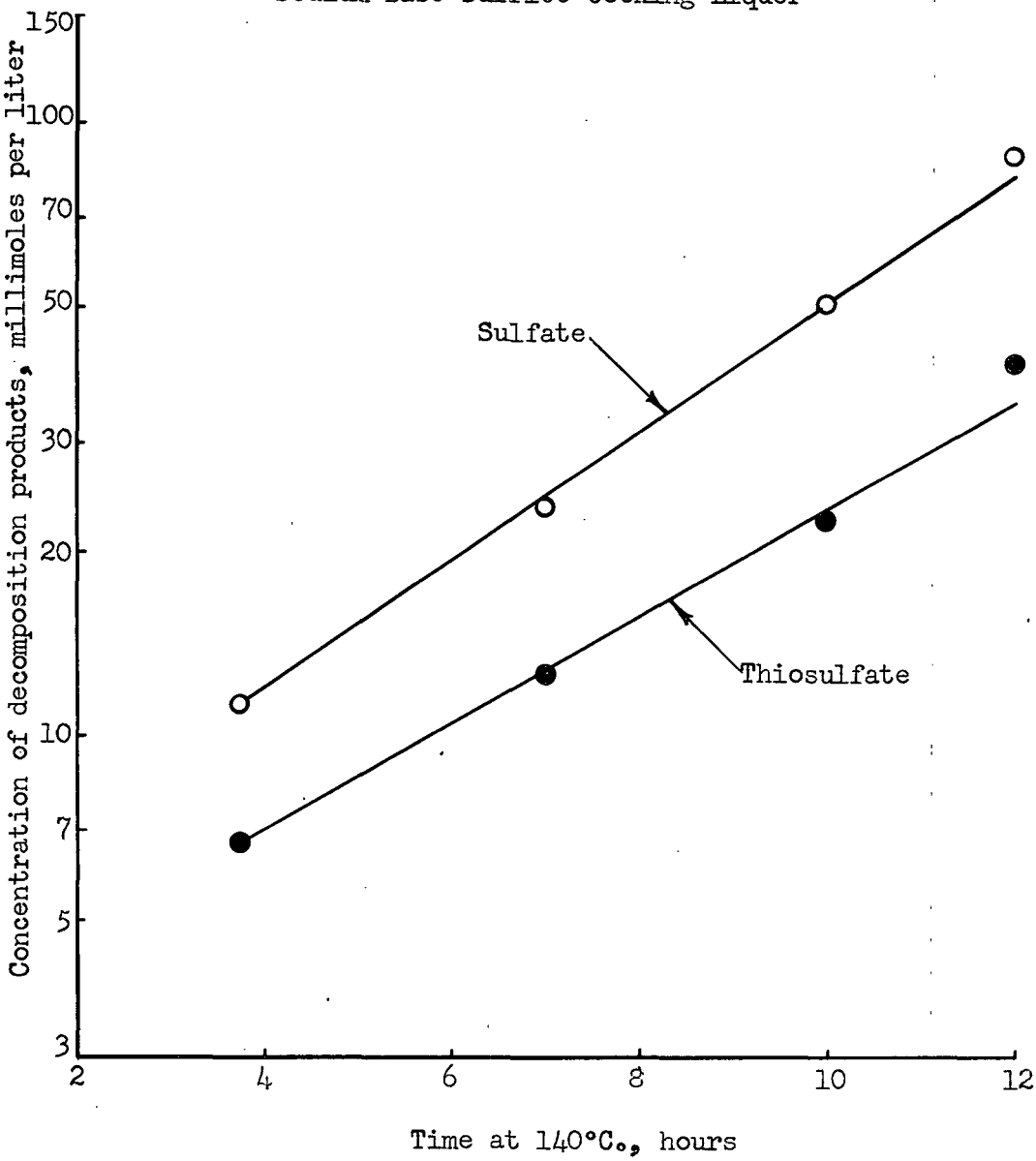
The rate of decomposition with dihydroquercetin is not as rapid as would be expected if this compound formed the theoretical amount of thiosulfate. After 10 hours, the only time at which direct comparison is possible, the thiosulfate-catalyzed liquor had 23.8% of the total sulfur existing as decomposition products. The corresponding value for the dihydroquercetin-catalyzed liquor is 11.1%. According to the equation for a first-order reaction, this indicates that the original thiosulfate concentration was only 46.5% as great in the latter series of cooks. This figure is in excellent agreement with the yields of quercetin obtained.

Figure 3

Concentration vs. Time
(Semilogarithmic Plot)

Dihydroquercetin-Catalyzed Decomposition of

Sodium-Base Sulfite Cooking Liquor



It is concluded that, under the conditions of these experiments, dihydroquercetin is quickly oxidized to quercetin with a yield of 45 to 50%. The accompanying reduction forms thiosulfate which decomposes the sulfite cooking liquor in an autocatalytic, first-order reaction.

$$2\ \text{Dihydroquercetin} + 2\ HSO_3^- \longrightarrow 2\ \text{Quercetin} + S_2O_3^{=} + 3H_2O$$

These conclusions disagree with the conclusions made by Kurth (17), who formed quercetin by refluxing dihydroquercetin at atmospheric pressure in a solution of 16% sodium bisulfite. Four successive batches of quercetin were obtained from the same bisulfite solution, and the individual yields, calculated on the basis of dihydroquercetin added at the beginning of each batch, were approximately the same. Kurth therefore concluded that the bisulfite lost very little of its effectiveness. However, the total amount of dihydroquercetin treated in the successive batches could theoretically reduce only about one-third of the bisulfite present, and liquor decomposition probably was not serious due to the low temperature. Therefore, a strong excess of bisulfite was probably present at all times. Also, if the quercetin yields from the individual batches were calculated on the basis of the total dihydroquercetin present, i.e., the sum of dihydroquercetin added at the beginning of the batch plus that which remained from previous batches, the effectiveness of the bisulfite solution dropped markedly. In effect, Kurth's data seem to support the conclusion that the bisulfite is changed. Along with this work,

Kurth conducted an additional series of experiments which showed that the degree of dihydroquercetin conversion depends on the bisulfite concentration of the solution.

The quercetin formed in these cooks was a bright yellow, fluffy, crystalline precipitate which was easily filtered from the cooled liquor. The precipitates and the filtered liquors were studied chromatographically to obtain visual purity estimates. The precipitates were quercetin ($R_f = 0$), in most cases totally free of dihydroquercetin ($R_f = 0.28$). The decomposed sulfite liquors, after filtration, gave strong tests for dihydroquercetin and faint tests for quercetin. The original dihydroquercetin had a very faint impurity ($R_f = 0.08$) which remained unchanged in the final solution. The final solutions also showed very faint spots at an R_f of 0.88. The chromatograms indicated that the only major organic reaction was the oxidation of dihydroquercetin to quercetin. However, other minor reaction products with the same chromatographic characteristics as the principal compounds could have remained undetected by this technique.

The purity of the mixture of the crude quercetin products formed in these experiments was determined by the ultraviolet absorbance method described by Naghski and Krewson (47). This procedure had been developed for the estimation of quercetin in mixtures containing quercetin and morin, a glycosidic quercetin derivative. Interfering compounds were assumed to be absent if the ratio of the absorbances at 375 and 362.5 millimicrons, respectively, fell within the limits

of 1.108 ± 0.020. The quercetin product obtained in this work had a ratio of 1.108. The weight of pure quercetin in the solution was then determined from the absorbance of the solution at 375 millimicrons and the absorptivity of pure quercetin, which Naghski and Krewson reported to be 80.0 at this wavelength. The quercetin product was found to be 94% pure by this method. The nature of the impurity was not determined.

OTHER COMPOUNDS AS DECOMPOSITION CATALYSTS

A number of different compounds were tested to determine their effects on the stability of sulfite cooking liquor. Single 10-hour cooks at 140°C. were made with phloroglucinol, resorcinol, catechin, formic acid, a mixture of free sugars and free sulfur.

The additives were reagent grade chemicals in each case, with the exception of the catechin, which was of somewhat questionable purity and structure. The catechin was over five years old and had been purchased as d-catechin. The sample had a light tan color—pure catechin crystals are white. It was found to be optically inactive and it had a melting point of 204°C. Chromatographically, the product seemed to be a pure compound with an R_f of 0.39. These properties correspond most closely to dl-catechin, one of the six stereoisomers of catechin, which has a melting point of 212-214°C. (48).

The sugar mixture contained 65% mannose, 25% xylose, and 10% galactose, on a molar basis. This is the approximate composition of

the sugar mixture which would be obtained from the hydrolysis of the hemicellulose portion of sprucewood.

These compounds were added to the digester in the dry, crystalline form in the manner described earlier for dihydroquercetin. Preliminary tests showed that these additives, with the exception of free sulfur, were readily soluble in the liquor. The free sulfur was obtained in lump form and was finely ground in a mortar prior to use. However, at the end of the 10-hour cooking period, a portion of the sulfur remained undissolved. Therefore, the effective concentration of the free sulfur could not be determined and this cook was only of qualitative value.

The results of these cooks, compared with those from pure liquor and liquor containing added thiosulfate, are shown in Table X.

The data of Table X show that dihydroquercetin is different from other well-known pulping inhibitors in its effect on the stability of sulfite cooking liquor. Phloroglucinol, resorcinol, and catechin do not promote bisulfite decomposition. Chromatographic comparisons of the original and final products showed that phloroglucinol and resorcinol were not changed by the cook. The catechin was partly changed. The chromatogram of the final liquor had a sharp dot (R_f = 0.39) which was similar to the original product; other marks, less clearly defined, were present at R_f values of 0.66, 0.75, and 0.89. No effort was made to identify these catechin reaction products.

TABLE X

COMPARISON OF DECOMPOSITION CATALYSTS

Cooking liquor: Sodium base, 1.40% combined SO_2, 6.00% total SO_2

Temperature Cycle: 1 1/2 hours to 140°, 10 hours at 140°C.

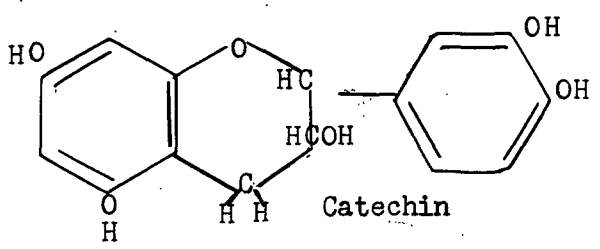
Additive	Additive Concentration Millimoles/liter	Theoretical Thiosulfate Formed from Additive Millimoles/liter	Decomposition Products Millimoles/liter Sulfate	Thiosulfate	Polythionate	Sulfur in Decomposition Products, %
Pure liquor	0.0	--	24.4	9.1	0.1	4.6
Phloroglucinol	14.0	--	25.0	10.7	--[a]	5.4
Resorcinol	14.0	--	20.8	7.6	1.2	4.4
Catechin	14.0	--	22.6	8.2	1.3	4.7
Dihydroquercetin	14.0	7.0	50.3	22.5	2.3	11.1
Formic acid	7.0	3.5	52.3	26.6	0.8	11.7
Free sulfur	7.0	--[b]	51.9	28.5	0.8	12.1
Thiosulfate	7.0	7.0	105	47.7[c]	5.7	23.8[c]
Free sugars	28.0	14.0	97	41.6	10.9	24.7
Formic acid	14.0	7.0	142	45.8	20.0	33.4

[a] The polythionate concentration was calculated to be about 8 millimoles per liter. This is obviously incorrect because it would show more reduction products than oxidation products. The phloroglucinol might have interfered with this analytical step.

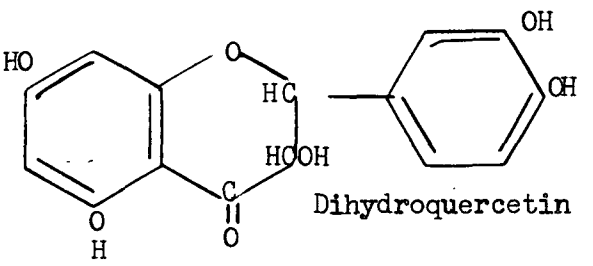
[b] The free sulfur was not completely dissolved.

[c] This figure includes the thiosulfate added to the original liquor.

The failure of catechin to reduce bisulfite is particularly interesting due to its close structural similarity to dihydroquercetin.



Catechin



Dihydroquercetin

Catechin, with two hydrogen atoms on the carbon atom in the 4-position, does not seem to be dehydrogenated by bisulfite. In contrast, dihydroquercetin, with a carbonyl group in the 4-position, loses two hydrogen atoms and reduces bisulfite to thiosulfate. This nonreactivity of catechin has been reported by Kurth (17), whose results were presented after this portion of the experimental work had been completed.

The reactions of various sugars with bisulfite have been studied by Hagglund and coworkers (30-32). The sugars are oxidized to their corresponding aldonic acids in yields of 45 to 50%, with the reduction of bisulfite to thiosulfate. The degree of oxidation of the free sugars, calculated from the data of Table X, was 52%. This figure is in reasonable agreement with Hagglund's results. The thiosulfate formed during the oxidation of sugars is probably the major cause of the bisulfite decomposition which occurs to a certain degree in all sulfite cooks. Also, sugars are probably a major factor in the difficulties encountered in the attempts to reuse sulfite spent liquors in the digester.

It has long been known that free sulfur promotes the decomposition of sulfite cooking liquor—this fact was reported by Klason (27) in 1910. The data obtained in this program substantiates this observation. The effect of free sulfur is undoubtedly due to the direct formation of thiosulfate catalyst through the combination of sulfur and bisulfate (26). Sulfite mills occasionally obtain burned cooks if free sulfur passes through the burner system and is dissolved in the cooking liquor. These burned cooks are probably the result of accelerated bisulfite decomposition which causes the base to be removed as calcium sulfate before delignification is complete.

The effect of formic acid on bisulfite decomposition was investigated by Stockman (33). He showed that two moles of formic acid reduce bisulfite to form one mole of thiosulfate. The data of Table X show that a formic acid concentration of 7 millimoles per liter has the same effect on bisulfite decomposition that would be expected from the equivalent amount of thiosulfate. However, formic acid, at a concentration of 14 millimoles per liter seems to have a somewhat greater effect than the equivalent thiosulfate.

In conclusion, any compound which causes the formation of thiosulfate in sulfite cooking liquor is a potential promoter of bisulfite decomposition. Most compounds form thiosulfate through the reduction of bisulfite. However, in the case of free sulfur, the thiosulfate is formed through a direct combination with the bisulfite (26).

THE EFFECT OF TEMPERATURE

Four cooks were made to determine the effect of temperature on the rate of bisulfite decomposition. The decomposition in these cooks was catalyzed by the addition of 7.0 millimoles per liter of thiosulfate to the starting liquor. The cooks were rapidly heated to the maximum temperature and held at the maximum temperature for 10 hours. The results are presented in Table XI.

TABLE XI

THE EFFECT OF TEMPERATURE

Cooking liquor: Sodium base, 1.40% combined SO_2, 6.00% total SO_2

Temperature, °C.	Decomposition Products Millimoles per Liter			Sulfur in Decomposition Products, % [a]
	Sulfate	Thiosulfate[a]	Polythionate	
130	24.5	16.4	0.4	6.3
135	52.1	28.4	2.9	12.9
140	105	47.7	5.7	23.8
145	402	186 [b]	10.0	86.9

[a] These figures include the thiosulfate added to the starting liquor.

[b] This figure is the sum of 9.2 millimoles per liter of thiosulfate and 177 milliatoms of free sulfur per liter. The sulfur is formed in the reaction: $S_2O_3^{=} + H^+ \rightleftharpoons S^o + HSO_3^-$.

These data show that between 130 and 140°C., the temperature coefficient of bisulfite decomposition is approximately four. Above 140°, the coefficient seems to be considerably greater. However, the temperature coefficient of bisulfite decomposition at temperatures over

140° cannot be determined from these data. The earlier study of thiosulfate-catalyzed decomposition showed that the decomposition follows the rules of a first-order reaction up to a sulfate concentration of about 105 millimoles per liter. The nature of the reaction in highly decomposed solutions is not known and the apparent increase in the temperature coefficient, at temperatures over 140°, might be misleading.

The temperature coefficient of the sulfite pulping reactions is generally considered to be about two. If the bisulfite decomposition reactions are the same in a conventional sulfite cook as they are in the absence of wood, a decrease in pulping temperature from 140 to 130° would decrease the pulping rate 50% and decrease the bisulfite decomposition rate 75%. Therefore, the detrimental effect of bisulfite decomposition in sulfite pulping should be eased by reducing the cooking temperature.

THE EFFECT OF DIHYDROQUERCETIN IN SULFITE PULPING

ANALYSIS OF WOOD

Pulping variables were studied in sulfite cooks conducted on sprucewood and Douglas-fir Sample B (275 years old). Samples of these wood were ground in a Wiley mill and the 40-60 mesh fraction was separated for analysis. The wood was successively extracted with alcohol-benzene (1:2) and hot water prior to the lignin determination. These analyses were conducted according to Institute Methods 11, 10, and 13,

respectively. The soluble lignin in the lignin filtrates was calculated at four different wavelengths. The results, shown in Table XII, are reported on the basis of the ovendry, unextracted wood.

TABLE XII

WOOD ANALYSIS

	Spruce	Douglas-fir Sample B
Alcohol-benzene solubility, %	2.20	4.66
Hot-water solubility, %	2.72	1.86
Insoluble lignin, %	26.4	28.2
Soluble lignin, %		
230 millimicrons	0.18	0.16
250 millimicrons	0.34	0.29
280 millimicrons	1.43	1.47
300 millimicrons	1.43	1.51

The lignin contents of these woods are in reasonable agreement with the results obtained by Brookbank (7). Brookbank obtained lignin contents of 27.6% and 28.6% for spruce and Douglas-fir heartwood, respectively. Brookbank reported the alcohol-benzene solubility of Douglas-fir to be 3.13%. Beuschlein (2) reported a value of 3.97% and Chidester and McGovern (8) obtained values between 3.2 and 5.9% from trees 98 years old and older.

The soluble lignin contents of spruce and Douglas-fir were found to be very low. In these analyses, the lignin in the unpulped wood probably had the same ultraviolet absorptivity curve as the spruce

native lignin which was used in these calculations. If these curves were the same, the minimum values of soluble lignin, which were those calculated at 230 millimicrons, represent the maximum possible concentrations of soluble lignin in the wood. The differences between the soluble lignin values calculated at different wavelengths are primarily the result of interfering materials.

The soluble lignin results are in reasonable agreement with the findings of Browning and Bublitz (43), who reported the soluble lignin content of spruce to be 0.9%, calculated at 280 millimicrons. However, the soluble lignin data in Table XII sharply disagree with the findings of Campbell and McDonald (49) and Von Wacek and Shroth (50) who reported spruce soluble lignin values of 5.8 and 5.5%, respectively.

In addition to the results presented in Table XII, several qualitative observations were made. The dried extracts were leached with boiling 95% ethanol and chromatograms of the solutions were prepared. The Douglas-fir alcohol-benzene extract gave a strong test for dihydroquercetin while the hot-water extract showed practically none of this material. Since the hot water is a suitable extractant for this compound (6,51), these results show that the alcohol-benzene extraction removes practically all of the dihydroquercetin originally present in the wood. The ferric chloride test for phenolic compounds and the zinc reduction test for 3-hydroxyflavanones (6) supported this conclusion.

The complete removal of dihydroquercetin by alcohol-benzene extraction is particularly pertinent to the findings of Beuschlein (2). Beuschlein extracted Douglas-fir sawdust with alcohol-benzene and found that it remained very difficult to delignify by the sulfite pulping process. This indicates that dihydroquercetin is not responsible for the major portion of the pulping resistance in Douglas-fir.

The chromatogram of the spruce alcohol-benzene extract had a streak between the R_f values of 0.64 and 0.70. This same mark was also observed on a chromatogram of a spruce ethanol extract. Several different spray reagents were used in an effort to characterize the spruce compound. The mark was quite clear with a ferric chloride-potassium ferricyanide mixture. The mark was colored by bis-diazotized benzidine, but it soon became indistinguishable as the background darkened with time. No markings could be observed with 2,4-dinitrophenylhydrazine. A sample of pinitol was placed beside the spruce extract on these chromatograms and no color was observed with any of the three spray reagents. The chemical nature of the spruce compound was not determined.

Separate tests showed that dihydroquercetin is present in both the heartwood and the sapwood from Douglas-fir. Chips from Douglas-fir Sample A were carefully sorted visually to obtain a small sample of sapwood. These chips were then ground in a Wiley mill and soaked overnight in 95% ethanol. The wood meal was filtered off and the extract was tested for dihydroquercetin. The sapwood extract gave a

positive chromatographic test for dihydroquercetin and it also gave a positive reaction to the zinc reduction test (6) for 3-hydroxyflavanones. In both cases, the test was weaker than that obtained with the heartwood extract. The presence of dihydroquercetin probably explains the yellow color of the pulps obtained by Chidester and McGovern (8) in their pulping studies of Douglas-fir sapwood.

DESCRIPTION OF COOKING CONDITIONS

The pulping experiments were designed to study the effect of dihydroquercetin on sulfite pulping, to study the pulping characteristics of Douglas-fir, and to compare the pulping characteristics of sprucewood containing dihydroquercetin with the pulping characteristics of untreated spruce and Douglas-fir.

The sulfite cooks conducted in this program are classified into three groups: the mixed pulping series, the spruce pulping series, and the Douglas-fir pulping series. The cooking conditions of each group are outlined below.

A. MIXED PULPING SERIES

Number of cooks: 12
Wood pulped: Spruce, spruce impregnated with dihydroquercetin, spruce impregnated with quercetin, Douglas-fir Sample B, and hot water-extracted Douglas-fir Sample B.
Cooking liquor: 1.25% combined SO_2, 5.00% total SO_2
Liquor ratio: 6 to 1
Temperature cycle: Schedule A. 1 hour to 90°, 3 hours from 90 to 115°, 2 hours from 115 to 140°, remainder of cook at 140°C.
Maximum pressure: 75 p.s.i. Cooks were blown from maximum pressure.
Digester: One-liter
Variables: Type of wood charged, time of cooking, and cooking liquor base.

B. SPRUCE PULPING SERIES

Number of cooks: 2
Wood pulped: Spruce
Cooking liquor: 1.25% combined SO_2, 6.0% total SO_2, sodium base
Liquor ratio: 6 to 1
Temperature schedule: Schedule C. 1 hour to 90°, 2 hours from 90 to 115°, 4 hours from 115 to 140°, 3 hours at 140°C.
Maximum pressure: 85 p.s.i. Cooks were blown from maximum pressure.
Digester: 38-liter
Variable: Concentration of thiosulfate in the cooking liquor

C. DOUGLAS-FIR PULPING SERIES

Number of cooks: 4
Wood pulped: Douglas-fir Sample B
Cooking liquor: 1.25% combined SO_2, 6.00% total SO_2
Liquor ratio: 6 to 1
Temperature cycle: Two cooks with schedule A, previously described. Two cooks with schedule B: 1 hour to 90°, 3 hours from 90 to 115°, 1 hour from 115 to 130°, remainder of cook at 130°C.
Maximum pressure: 85 p.s.i. for schedule A with 140° maximum temperature. 75 p.s.i. for schedule B with 130° maximum temperature. Cooks were blown from maximum pressure.
Digester: 38-liter
Variables: Cooking liquor base, temperature schedule and time of cooking.

DIHYDROQUERCETIN IN SULFITE PULPING

Dihydroquercetin as a Pulping Inhibitor

Six sulfite cooks of the mixed pulping series were conducted to study the effect of dihydroquercetin on the sulfite pulping of spruce. Three cooks were made with untreated spruce, and these cooks were then repeated using sprucewood chips that had been impregnated with dihydroquercetin. The results of these cooks are presented in Table XIII.

TABLE XIII

THE EFFECT OF DIHYDROQUERCETIN ON SULFITE PULPING

Mixed pulping series cooking conditions

Cook	A	B	C	C	G	I
Dihydroquercetin, %	None[a]	3.4	None[a]	3.2[b]	None	3.3[c]
Cooking liquor base	Na	Na	Ca	Ca	Ca	Ca
Total cooking time, hr.	9	9	9	9	10½	10½
Drained liquor						
pH	1.53	1.49	1.40	1.38	1.19	1.19
Sulfate, mmol./l.	28.8	25.9	8.9	10.2	33.5	44.4
Thiosulfate, mmol./l.	15.0	19.4	14.3	18.2	28.4	25.6
Combined SO_2, %	0.56	0.63	0.47	0.47	-0.09	-0.17
Free SO_2, %[2]	2.72	2.64	1.93	2.23	1.40	1.01
Expressed liquor						
pH	4.00	3.92	3.70	3.67	1.51	--
Sulfate, mmol./l.	33.6	30.8	27.9	31.2	48.3	--
Thiosulfate, mmol./l.	18.0	21.6	18.4	22.8	21.8	--
Combined SO_2, %	0.42	0.50	0.39	0.39	-0.05	--
Pulp						
Total yield, %	49.9	51.1	50.1	50.5	44.0	46.1
Permanganate number	15.0	26.6	17.7	40.9	5.2	14.8
Alcohol solubility, %	1.75	1.73	1.55	1.51	0.89	1.09
Insoluble lignin, %	1.2	4.1	2.2	7.0	0.3	1.8
Soluble lignin, %	3.6	3.0	3.1	2.6	1.0	1.6
Total lignin, %	4.8	7.1	5.3	9.6	1.3	3.4
N on lignin yield, %	47.5	47.5	47.5	45.6	43.4	44.6
Lignin, % on ovendry wood	2.4	3.6	2.7	4.8	0.6	1.6

[a] Chips were given impregnation treatment with water alone.
[b] A dihydroquercetin content of 3.2%, with a liquor ratio of 6 to 1, is equivalent to a concentration of 17.5 millimoles per liter.
[c] Chips were impregnated with 3.0% dihydroquercetin. The additional 0.3% was added to the cooking liquor.

The data in Table XIII verify the findings of Pew (6), who reported that dihydroquercetin is a pulping inhibitor. Pew found that 1.7% dihydroquercetin, impregnated into the wood, increased the insoluble lignin content of the pulp from 1.8% to 6.4%. These data are similar to those obtained with Cooks C and D, although the cooking conditions were somehwat different and the dihydroquercetin content was greater than used by Pew. A portion of the dihydroquercetin in Cooks B, D, and I did not enter into a permanent combination with other compounds. In Cooks B and D, over 10% of the additive precipitated from the final liquor as quercetin after standing for several days. Also, chromatographic studies of the final liquors from these cooks showed that unchanged dihydroquercetin was present.

Dihydroquercetin is not as effective a pulping inhibitor as phloroglucinol or resorcinol. Erdtman (21) reported that 1.1% resorcinol, impregnated into spruce chips, caused the lignin content of the resulting pulp to be increased from 4% to 17.5%. This concentration of resorcinol corresponds to 3.0% dihydroquercetin, on a molar basis. Pew (6) showed that 1.7% dihydroquercetin, added to the cooking liquor, increased the lignin content of the pulp from 1.8% to 4.2%. An equimolar amount of resorcinol increased the lignin content to 9.0%.

The data of Table XIII show that the pulping resistance caused by dihydroquercetin is slightly reduced by the use of a sodium-base working liquor. In cooks B and D, the difference between the total lignin contents of the pulps was not great, and might be partially

attributed to the improved pulping characteristics which are experienced with most species of wood upon changing from calcium- to sodium-base cooking liquors.

Dihydroquercetin as a Phenolic Inhibitor

Erdtman (19-21) showed that polyphenolic compounds, particularly these with hydroxyl groups in a 1-3 configuration, tend to inhibit sulfite pulping. Dihydroquercetin meets these structural requirements. Erdtman has suggested that the phenolic compounds condense with the lignin in the wood to form an "insoluble,——absolutely nondisintegrable material." After phenolization has occurred, "only sugar and easily hydrolyseable polysaccharides are removed during the cooking process, leaving cellulose and phenol lignin undissolved" (19).

The data of Table XIII show that dihydroquercetin does not react with spruce lignin to form an insoluble lignin product which cannot be removed by extending the cook. By extending the cooking time from 9 hours to 10-1/2 hours, the lignin content of the pulp, calculated on the basis of the ovendry wood, was reduced from 4.8% to 1.6%. The corresponding lignin contents of the pulps from untreated sprucewood were 2.7% and 0.6%, respectively. (See Cooks C, D, G, and I.) These data show that, although dihydroquercetin seems to retard the lignin removal, it does not form an insoluble lignin-inhibitor complex which cannot be removed. Therefore, dihydroquercetin does not conform to Erdtman's description of phenolic inhibitors.

Erdtman's description of an "absolutely nondisintegrable" lignin-inhibitor complex seems to be based on the results of a single experiment (21). The study involved a series of two-stage cooks with spruce, spruce impregnated with different amounts of resorcinol, and pine. The chips were vacuum-impregnated with a calcium-base cooking acid and then cooked in the conventional manner for 5-1/2 hours——3-1/2 hours to 135°, and 2 hours at 135°C. The chips were removed from the digester and, by a series of washings with acid and NaCl solutions, the insoluble calcium lignosulfonates were converted to sodium lignosulfonates. These chips were then cooked for various time intervals, up to 24 hours, in distilled water at 100°C., and the lignin contents were determined. The pine, along with the spruce with 10% resorcinol, showed practically no removal of lignin by the hot water treatment. The hot water treatment reduced the lignin content of the inhibitor-free spruce from 19 to 6% in 8 hours, and to 5% in 24 hours. The lignin content of the spruce treated with 1% resorcinol, which was 25% prior to the water treatment, was reduced to 18% in 8 hours and to 16% in 24 hours. These data show the presence of a lignin-inhibitor complex which is insoluble in boiling distilled water. However, the degree of its resistance to sulfite cooking liquor cannot be determined from Erdtman's results. A lignin-inhibitor complex might be removed by sulfite cooking liquor if given sufficient time.

Migita and coworkers (18) have obtained data which suggests that dihydroquercetin might not act as a phenolic inhibitor. They concluded

that the lignin-inhibitor condensation does not occur to any great extent when dihydroquercetin is cooked in the presence of isolated native lignin.

In conclusion, dihydroquercetin does not cause the formation of a "phenolized" lignin which cannot be removed by sulfite pulping. The presence of this compound seems to retard the removal of lignin from the wood and this might be due to some type of interaction with the lignin. However, the substantial removal of lignin from spruce chips impregnated with dihydroquercetin, during the latter portion of the cook, indicates that serious phenolization does not occur.

Dihydroquercetin as a Bisulfite Decomposition Catalyst

Retarded Bisulfite Decomposition in the Presence of Wood

The thiosulfate, sulfate, and combined sulfur dioxide analysis give measures of the degree of bisulfite decomposition in a sulfite cook. The thiosulfate concentration can be used to estimate bisulfite decomposition in the presence of available base in the cooking liquor—the acidic conditions which accompany base depletion promote the breakdown of thiosulfate into free sulfur and sulfurous acid.

The sulfate concentration is a measure of the bisulfite decomposition in sodium-base cooks. In calcium-base cooks, the soluble sulfate concentration remains at about 10 millimoles per liter until the base nears exhaustion and free sulfuric acid is formed. The increase of total sulfate concentration in calcium-base cooks is similar to that

in sodium-base cooks (52), but due to the low solubility of calcium sulfate, it precipitates on the pulp or on the heating surface and is only partially represented in the sulfate analysis of the liquor. Considerable amounts of precipitate were present on the cooked chips in the 10-1/2 hour calcium-base cooks G and I. The precipitate could not be detected visually in the 9-hour cooks.

The combined sulfur dioxide concentration is a measure of the cooking liquor base consumption. The two main sources of base demand are the lignosulfonic acids and the acids formed in the bisulfite decomposition. Therefore, at a given degree of sulfonation, the combined sulfur dioxide concentration can be used as a measure of the bisulfite decomposition.

The effect of dihydroquercetin on the bisulfite decomposition in a sulfite cook is shown in Table XIII. The 9-hour cooks, B and D, had higher thiosulfate concentrations than the corresponding cooks, A and C, which did not contain dihydroquercetin. However, this trend was not shown by the sulfate and combined sulfur dioxide analyses. Comparison of Cooks G and I indicates that dihydroquercetin causes increased bisulfite decomposition if the cooking times are extended. However, the differences are quite small and their effects on the pulping reactions are probably of minor consequence.

The formation of calcium sulfate or insoluble quercetin within the chips could retard pulping by blocking the pores of the chips to prevent the diffusion of the cooking liquor into, or reaction products

out of the chips. Such a phenomenon would be accompanied by an increase in the difference between the compositions of the expressed and drained liquors. The comparison of the expressed and drained liquor compositions, shown in Table XIII, fails to show any evidence of blocked diffusion in the cooks containing dihydroquercetin.

The observed behavior of calcium sulfate and quercetin in these sulfite cooks indicates that these compounds do not form precipitates in the chip pores. The 9-hour, calcium-base Cooks C and D had expressed liquor sulfate concentrations approximately the same as those in the corresponding sodium-base Cooks A and B. The calcium-base expressed liquors were transparent when removed from the pulp and upon standing, a large amount of precipitate was formed. This precipitate was presumably calcium sulfate, possibly accompanied by calcium sulfite. These facts suggest that the expressed liquors are highly supersaturated with sulfate, which does not precipitate until the liquor has diffused out of the chips. The quercetin, formed from the oxidation of dihydroquercetin, is somewhat soluble in sulfite spent liquor under cooking conditions—a quercetin precipitate separated from both the expressed and drained liquors of Cooks B and D after standing for several days. Therefore, the precipitation of either quercetin or calcium sulfate in the chip pores seems unlikely.

In summary, the data show that, although dihydroquercetin is a strong promoter of bisulfite decomposition in the absence of wood, it has only a small effect on bisulfite decomposition in the presence of

wood. There is no evidence of this compound causing the formation of a precipitate which might block the chip pores to prevent diffusion. Dihydroquercetin-catalyzed bisulfite decomposition is therefore responsible for very little, or none, of the pulping resistance of Douglas-fir.

Explanation of the Retarded Bisulfite Decomposition

Dihydroquercetin exerts a strong effect in promoting bisulfite decomposition in the absence of wood. If bisulfite decomposition would proceed in the same manner in the presence of wood, a small amount of dihydroquercetin could have a very deleterious effect. However, the data in Table XIII show that this does not take place. The presence of wood seems to repress bisulfite decomposition.

Dihydroquercetin is an indirect decomposition catalyst through its reduction of bisulfite to thiosulfate. Data have been obtained to show that the wood, or its reaction products, removes thiosulfate from the cooking liquor during the early portion of the cooking cycle. The removal of the thiosulfate catalyst retards the bisulfite decomposition that would have occurred in the absence of wood.

Two sodium-base cooks of sprucewood chips were conducted in the 38-liter digester and liquor samples were withdrawn at various time intervals throughout the cooks. The only difference between the conditions of the two cooks was the addition of 7 millimoles per liter of thiosulfate to the starting liquor of Cook II. The reduction of the thiosulfate concentration by the wood is shown in the data of Table XIV, presented graphically in Figure 4. The cooks were approximately the

same in their curves of combined sulfur dioxide and sulfate *vs.* time. These data are shown in Appendix A.

TABLE XIV

THE EFFECT OF THIOSULFATE ON THE SULFITE PULPING OF SPRUCEWOOD

Spruce pulping series cooking conditions: 140°C. maximum temperature, 10-hour cook.

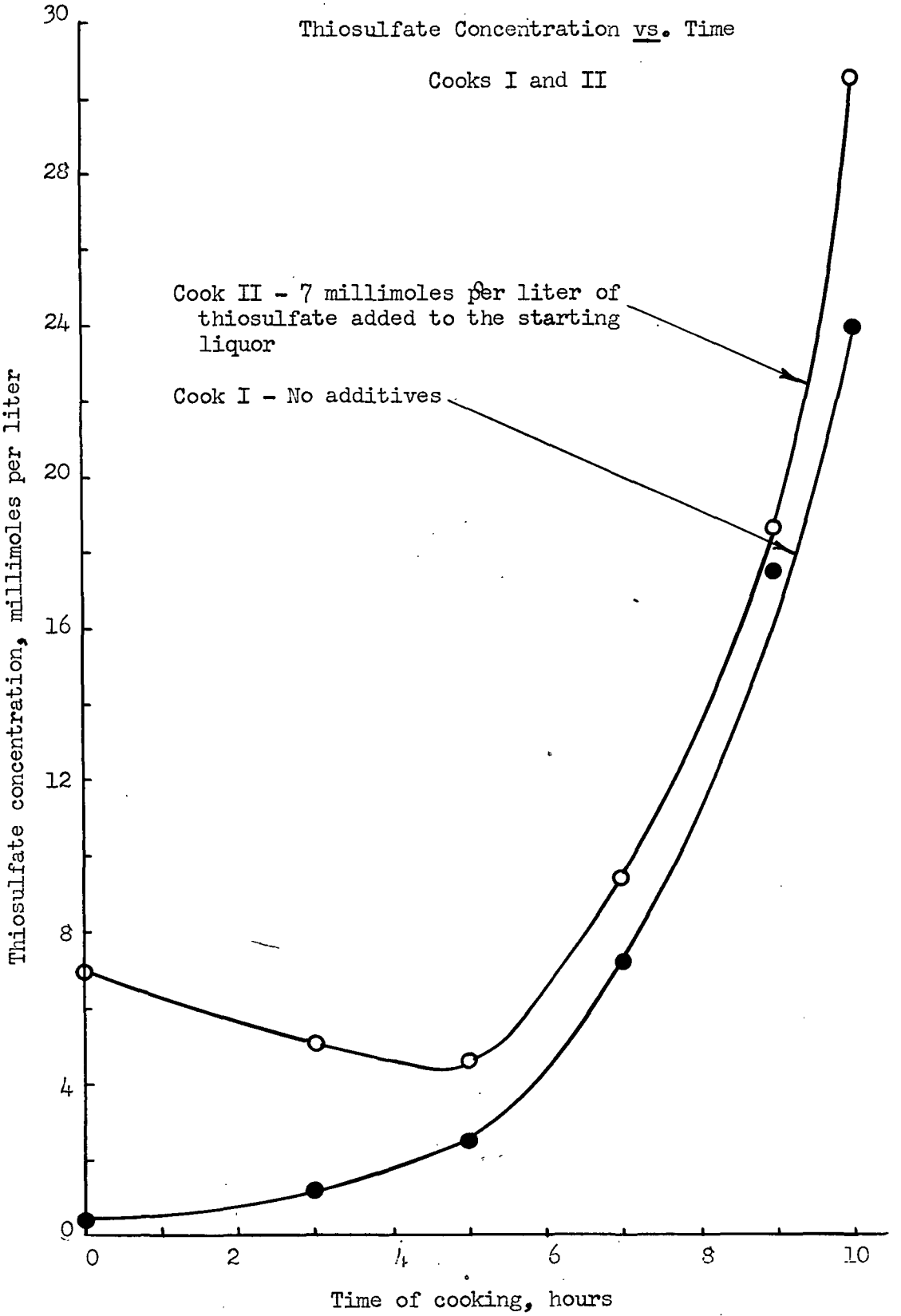
Cook	I	II
Thiosulfate added to liquor	None	7 Millimoles per liter
Screened yield, %	44.5	44.9
Screenings, %	0.8	0.4
Permanganate number	5.0	6.0
G.E. Brightness, %	64.3	62.9
Thiosulfate concn., mmol./l		
0 hour	0.4	7.0
3	1.2	5.1
5	2.5	4.6
7	7.2	9.4
9	17.5	18.7
10	23.9	30.6

The consumption of thiosulfate by the wood seems to explain the failure of low concentration of thiosulfate to promote serious bisulfite decomposition in a conventional sulfite cook. Stockman (33) showed that formic acid, equivalent to 5-1/2 millimoles per liter of thiosulfate, caused serious decomposition in the absence of wood, but had little effect on a calcium-base cook of sprucewood. However, with a formic acid concentration equivalent to 22 millimoles per liter of thiosulfate, the cooks were seriously damaged, and in some cases, "burned" cooks

Figure 4

Thiosulfate Concentration vs. Time

Cooks I and II



resulted. In the latter case, the wood probably did not remove enough thiosulfate to prevent serious bisulfite decomposition.

The amount of thiosulfate formed by the oxidation of dihydroquercetin in any Douglas-fir cook will probably not exceed 8 millimoles per liter. This concentration of thiosulfate would be formed by 2.4% dihydroquercetin in the wood, complete oxidation of this compound, and a liquor ratio of 5 to 1. The wood consumes enough of this thiosulfate to prevent serious acceleration of the natural bisulfite decomposition which occurs in all sulfite cooks. A thiosulfate concentration of 20 millimoles per liter would probably cause serious damage to the pulp.

The mechanism by which wood, or its reaction products, causes the reduction of thiosulfate concentration is not known. Alkaline thiosulfate has been reported to be a pulping agent and the pulps from such cooks contained up to 3% sulfur (53). This suggests that, under alkaline conditions, the thiosulfate might react with the lignin. There is no knowledge of a thiosulfate-lignin reaction in an acidic sulfite cook. Judging from the reduction of the thiosulfate concentration in the early portion of a sulfite cook, it is possible that the thiosulfate might react with the lignin in a reaction which competes with the first sulfonation step. In this way, the thiosulfate might cause the formation of a lignin product which is difficult to remove by sulfite pulping. but the results of the spruce cooks shown in Table XIV indicate that such an effect is not sufficiently great to explain the difficulty in Douglas-fir pulping.

PULPING COMPARISONS WITH DOUGLAS-FIR

The Slow Removal of Douglas-Fir Lignin

Two calcium-base cooks of Douglas-fir were conducted to allow comparison of the pulping characteristics of Douglas-fir with the pulping characteristics of spruce and spruce impregnated with dihydroquercetin. The data from these cooks, along with that from other pertinent calcium-base cooks, are presented in Table XV.

The precipitate which occurs in the calcium-base pulping of Douglas-fir was found in all three of the 10-1/2 hour cooks, although the Douglas-fir Cook F seemed to have more precipitate than the others. The spruce cooks had greater degrees of lignin removal and, under these conditions, a greater portion of the calcium might have been tied up with the soluble lignosulfonates, leaving less calcium available for precipitation as calcium sulfate.

The pulp from the spruce chips impregnated with dihydroquercetin, and the Douglas-fir pulp, had a bright yellow-orange color when the cooks were blown. After repeated washings with hot water, the color was changed to a dull, yellowish tan. After the moist pulps had been allowed to stand for several days in sealed polyethylene bags, the Douglas-fir pulps lost almost all of their yellow color, while the spruce-dihydroquercetin pulps remained quite yellow. The pulps from the 9-hour cooks retained more of the yellow color than did those from the 10-1/2-hour cooks.

TABLE XV

COMPARISON OF PULPING CHARACTERISTICS

Mixed pulping series cooking conditions

Cook	C	G	D	I	E	F
Wood species	Spruce[a]	Spruce	Spruce	Spruce	D.-Fir	D.-Fir
Dihydroquercetin added, %	None	None	3.2	3.3[b]	None	None
Time of cooking, hr.	9	10-1/2	9	10-1/2	9	10-1/2
Drained liquor						
pH	1.40	1.19	1.38	1.19	1.38	1.39
Sulfate, mmol./l.	8.9	33.5	10.2	44.4	10.3	35.9
Thiosulfate, mmol./l.	14.3	28.4	18.2	25.6	16.8	14.8
Combined SO_2, %	0.47	-0.09	0.47	-0.17	0.46	-0.07
Free SO_2, %	1.93	1.40	2.23	1.01	2.46	1.38
Expressed liquor						
pH	3.70	1.51	3.67	--	4.35	1.73
Sulfate, mmol./l.	27.9	48.3	31.2	--	25.4	49.5
Thiosulfate, mmol./l.	18.4	21.8	22.8	--	22.0	12.9
Combined SO_2, %	0.39	-0.05	0.39	--	0.43	-0.09
Pulp						
Total yield, %	50.1	44.0	50.5	46.1	59.0	50.1
Permanganate number	17.7	5.2	40.9	14.8	>45	38.0
Alcohol solubility, %	1.55	0.89	1.51	1.09	0.78	1.11
Insoluble lignin, %	2.2	0.3	7.0	1.8	14.8	8.3
Soluble lignin, %	3.1	1.0	2.6	1.6	3.2	2.2
Total lignin, %	5.3	1.3	9.6	3.4	18.0	10.5
Nonlignin yield, %	47.5	43.4	45.6	44.6	48.3	44.9
Lignin, % on ovendry wood	2.7	0.6	4.8	1.6	10.6	5.3

[a] Chips were given the impregnation treatment with water alone.
[b] The chips were impregnated with 3.0% dihydroquercetin. Dihydroquercetin (0.3%) was added to the cooking liquor.

Chromatographic analyses showed that dihydroquercetin was not present in the spent liquors from the Douglas-fir cooks. The chromatograms showed a mark at an R_f of 0, which probably was quercetin. However, certain other wood compounds also give a mark in this position. The alcohol-benzene and the hot water extracts from both spruce and Douglas-fir contain a small amount of material which is not moved by the 0.01 N hydrochloric acid developer, but is slightly colored by the spray reagent. The data of Table XV serve as the basis for five conclusions:

1. The rate of bisulfite decomposition in the pulping of Douglas-fir was approximately the same as that which occurred in the pulping of spruce.
2. The rates of carbohydrate removal from these samples of spruce and Douglas-fir were approximately the same.
3. The lignin in the Douglas-fir was more difficult to remove than that in the spruce.
4. The lignin in Douglas-fir did not form an insoluble complex with an inhibitor, judging from the large amount of lignin removed during the last 1-1/2 hour portion of the cook.
5. There was no indication of a precipitate blocking the pores of Douglas-fir chips to prevent diffusion.

The resistance of Douglas-fir to calcium-base sulfite pulping is not the result of accelerated liquor decomposition—the rate of bisulfite decomposition is approximately the same as that in the pulping of spruce, an easily pulped species. The difficulty in Douglas-fir pulping

is the slow rate of lignin removal which allows the bisulfite decomposition, which proceeds at a normal rate, to attain serious proportions before the delignification is completed.

Any sulfite cook might be considered a race between two over-all reactions—the desired series of reactions which result in wood delignification, and the bisulfite decomposition reactions. The decomposition, which occurs primarily toward the end of the cook, forms sulfuric acid which precipitates as calcium sulfate and thereby reduces the supply of available calcium. A satisfactory sulfite cook is characterized by the approximate completion of the delignification before the bisulfite decomposition becomes serious. In a calcium-base cook of spruce, the delignification is essentially completed before the sulfuric acid formation becomes a serious competitor for base. The Douglas-fir lignin removal is only partially completed when the available calcium is precipitated by the sulfate formed in the bisulfite decomposition.

The desirability of a pulpwood for sulfite pulping might also be expressed in terms of the relative rates of carbohydrate and lignin removal. The rate of carbohydrate removal is probably important because of its effect on the rate of bisulfite decomposition through the formation of thiosulfate catalyst in the reaction between bisulfite and sugars. The rapid removal of carbohydrate material in a Douglas-fir cook, relative to the rate of lignin removal, is thereby a probable factor in the difficulty of pulping this species.

In conclusion, the lignin in Douglas-fir can be removed by the conventional sulfite pulping process, but the rate of lignin removal is sufficiently slow to cause difficulty. The major portion of the pulping resistance of Douglas-fir cannot be attributed to phenolization of the lignin or to accelerated bisulfite decomposition. The dihydroquercetin might be a factor in the slow removal of the lignin, but the serious pulping resistance of dihydroquercetin-free Douglas-fir, reported by Beuschlein (2), indicates that the major portion of the pulping difficulty cannot be attributed to the presence of this compound.

Comparison of the Sulfur Contents of Lignins

Several tests were made to compare the sulfur content of the lignin remaining in the Douglas-fir and the spruce pulps. This was done in the hope of learning the reasons for the slow rate of lignin removal in the Douglas-fir cooks.

Two special calcium-base cooks of spruce chips were conducted to obtain lignin contents, based on the original wood, approximately the same as those obtained from the 9-hour and the 10-1/2-hour calcium-base cooks of Douglas-fir. The sulfur content of the lignin was calculated from the sulfur content of the pulp and the lignin content of the pulp. This calculation was based on the assumption that all of the sulfur exists in the lignin. The results of these tests are presented in Table XVI.

TABLE XVI

SULFUR CONTENT OF LIGNIN IN PULP

Mixed pulping series cooking conditions

Cook	J	K	E	F
Wood species	Spruce	Spruce	D.-Fir	D.-Fir
Time of cooking, hr.	6-1/2	7-1/2	9	10-1/2
Total yield, %	65.7	57.2	59.0	50.1
Sulfur, %, in pulp	0.92	0.58	0.99	0.69
Insoluble lignin, % in pulp	13.1	6.3	14.8	8.3
Insoluble lignin, % on ovendry wood	8.6	3.6	8.7	4.2
Sulfur, % on insoluble lignin	7.1	9.2	6.7	8.4
Soluble lignin, % in pulp [a]	6.9	5.4	3.2	2.2
Total lignin, % in pulp	20.0	11.7	18.0	10.5
Total lignin, % on ovendry wood	13.1	6.8	10.6	5.3
Sulfur, % on total lignin	4.6	4.9	5.5	6.6

[a] Calculated from the absorbance at 230 millimicrons

The high sulfur values in the lignin, calculated on the basis of the insoluble lignin, show that the 72% sulfuric acid lignin determination probably did not include all of the lignin in the pulp. Brauns (54-55) has reported that the minimum sulfur content required to render the lignin soluble is about 3.5%. Upon additional cooking, lignosulfonic acids with about 6.5% sulfur are formed. The sulfur contents of the lignin reported in Table XVI, calculated on the basis of the insoluble lignin, are considerably higher than these figures. The sulfur contents, calculated on the basis of the total lignin, are in general agreement with the values reported by Brauns. However, the total lignin determination is also subject to serious errors.

The conclusions regarding the sulfur in the different lignins are dependent on the lignin analysis used in the calculations. If the insoluble lignin calculations are considered to be correct, the sulfur contents of spruce lignin and Douglas-fir lignin are nearly the same at comparable lignin yields, based on the original wood. However, the Douglas-fir lignin required considerably longer cooking times to obtain a given sulfur content. It might then be concluded that the Douglas-fir lignin is more difficult to sulfonate.

If the calculations are based on the total lignin content, the pulps show an orderly increase of lignin sulfur content with time. This trend suggests that the Douglas-fir lignin is sulfonated satisfactorily. In this case, the difficulty of Douglas-fir lignin removal might be associated with the hydrolysis and the dissolving of the sulfonated lignin. Either of the two hypotheses would seem to be in agreement with the known fact that Douglas-fir can be successfully delignified by a cooking liquor containing a high concentration of free sulfur dioxide (5, 7, 15).

It can be concluded from these data, that the Douglas-fir lignin is sulfonated in a conventional sulfite cook. If serious phenolization of the lignin had occurred, the Douglas-fir lignin sulfur content would have been considerably lower.

QUERCETIN IN SULFITE PULPING

Quercetin as a Pulping Inhibitor

Quercetin is formed in all sulfite cooks which originally contained dihydroquercetin. A 9-hour calcium-base sulfite cook of spruce chips, impregnated with 2.1% quercetin, was conducted to determine if this compound might contribute to the pulping resistance. The quercetin used in this cook was recovered from earlier cooks of dihydroquercetin in the absence of wood, and the purity was 94%. The impregnation procedure was slightly different from that described earlier for dihydroquercetin, in that a methanol solution of quercetin was used. The results of the quercetin cook, compared with results from similar cooks of untreated spruce, and spruce impregnated with dihydroquercetin, are presented in Table XVII.

The data of Table XVII show that quercetin, like dihydroquercetin, acts as a mild pulping inhibitor and causes an increase in the permanganate number and the lignin content of the resulting pulp. The effect of quercetin should be the same as the effect of dihydroquercetin, except, in the case of the latter compound, a portion of the bisulfite is reduced to thiosulfate. Previous results have shown that the thiosulfate formation, accompanying the oxidation of dihydroquercetin, has little effect, and, therefore, quercetin would be expected to contribute to pulping resistance. The data of Table XVII show that quercetin contributes to pulping resistance, although quantitative estimates of its effect cannot be made from these results.

TABLE XVII

QUERCETIN AS A PULPING INHIBITOR

Mixed pulping series cooking conditions

Cook	C	L	D
Additive	None	2.1%[a] Quercetin	3.2%[a] Dihydroquercetin
Final drained liquor			
Sulfate, mmol./l.	8.9	10.1	10.2
Thiosulfate, mmol./l.	14.3	20.5	18.2
Combined SO_2, %	0.47	0.44	0.47
Quercetin precipitate	--	No	Yes
Pulp			
Total yield, %	50.1	51.4	50.5
Permanganate number	17.7	36.2	40.9
Alcohol solubility, %	1.55	1.04	1.51
Insoluble lignin, %	2.2	4.3	7.0
Soluble lignin, %	3.1	3.0	2.6
Total lignin, %	5.3	7.3	9.6
Nonlignin yield, %	47.5	47.6	45.6
Lignin, % on ovendry wood	2.7	3.8	4.8

[a] A 2.1% quercetin content corresponds to 11.6 millimoles per liter. A 3.2% dihydroquercetin content corresponds to 17.5 millimoles per liter.

The Effect of Quercetin on Pulp Analyses

Sulfite pulps, obtained from cooks containing dihydroquercetin or quercetin, have the yellow color of quercetin when the cook is blown. Upon standing, this color changes to a dull yellow or tan. These pulps, unlike other spruce pulps, give an immediate, dark color with ferric chloride. This shows the presence of phenolic material which is probably quercetin.

The yellow color of these pulps cannot be removed by repeated washings with hot water, or by extraction with alcohol, acetone, or a 9:1 mixture of 95% ethanol and concentrated hydrochloric acid. The final extracts are colorless or very slightly yellow.

The yellow pulp which was treated with the hydrochloric acid-ethanol solution, lost most of its color due to the high acidity. After standing for 48 hours, the pulp was filtered from the solution, washed with 95% ethanol, and reslurried in distilled water. Several drops of 10% sodium hydroxide were added to make the solution slightly alkaline to litmus paper and the pulp obtained the deep orange color indicative of quercetin. The failure of acidic alcohol to remove the color suggests that the color is not due to a calcium-quercetin complex. Kurth (17) hypothesized that the pulping resistance of Douglas-fir might be due to a calcium-quercetin complex.

The reasonable certainty that quercetin is present in pulps from Douglas-fir and sprucewood impregnated with dihydroquercetin, led to the investigation of the effect of quercetin on the permanganate number and the lignin determination. The permanganate consumptions of dilute solutions of quercetin were determined in the absence of pulp. A weighed amount of the quercetin product, of 94% purity, was dissolved in a liter of water containing 1 ml. of 10% sodium hydroxide. Different volumes of this solution were drawn out and the permanganate consumptions were determined, using the standard permanganate number procedure. The results are shown in Table XVIII.

TABLE XVIII

THE PERMANGANATE CONSUMPTION OF QUERCETIN

Institute Method 410. 25 ml. of 0.1 N $KMnO_4$ added

Grams of Quercetin Added	Ml. of 0.1 N $KMnO_4$ Consumed	Grams of 94% Quercetin per Equivalent of $KMnO_4$ Consumed
0.00462	6.2	7.46
0.00925	12.4	7.46
0.01387	17.4	7.95
0.01850	21.7	8.40

The data of Table XVIII show that quercetin reacts with permanganate quantitatively, providing a sufficient excess of permanganate is present. The results show that a quercetin content of 0.75% in the pulp would increase the permanganate number 10 points. This suggests that the permanganate number might be an unreliable measure of the degree of cooking in Douglas-fir pulps or other pulps containing quercetin. However, Migita and coworkers (18) concluded that the yellow sulfite pulps obtained from Japanese larch, which contains dihydroquercetin, did not contain over 0.12% quercetin. This amount of quercetin would cause an error of less than 2 points in the permanganate number.

Quercetin, in the absence of pulp, has no effect on the insoluble lignin determination, using the 72% sulfuric acid method. Two determinations were conducted with 0.0548 grams of 94% quercetin in 20 ml. of 72% sulfuric acid. The acid slowly changed the color from yellow to a grayish-tan, and, after several hours the material was completely

dissolved. The ultraviolet absorbance curves for the solutions were very different from the curve obtained with the original quercetin product, indicating that the quercetin was chemically changed. These ultraviolet absorbance curves are shown in Figure 5.

Quercetin, in the presence of pulp containing lignin, increases the results of the lignin determination. Pulp C, with an insoluble lignin content of 2.2%, had a lignin content of 4.5% when the determination was conducted in the presence of 6.0% quercetin, based on the ovendry, quercetin-free pulp. The lignin filtrates had ultraviolet absorbance curves which did not show the typical maximum at 280 millimicrons. These curves are shown in Figure 5. The quercetin increased the soluble lignin content, calculated at 280 millimicrons, from 3.7% to 9.2%.

The lignin determinations on pulps B and D (spruce impregnated with dihydroquercetin), shown in Table XIII, were probably quite accurate. The lignin filtrate ultraviolet absorbance curves were the same as those obtained with the corresponding pulps that did not contain quercetin. Two of these curves are shown in Figure 6. Also, the insoluble lignin values for pulps B and D were slightly lower than those obtained from the corresponding pulps without quercetin. If sufficient quercetin were present to cause a sizable difference in either the soluble or the insoluble lignin determinations, there probably would have been a difference in the ultraviolet absorbance curves of the lignin filtrates.

Figure 5

Ultraviolet Absorbance vs. Wavelength

Absorbance Curves of Quercetin and Lignin Filtrates

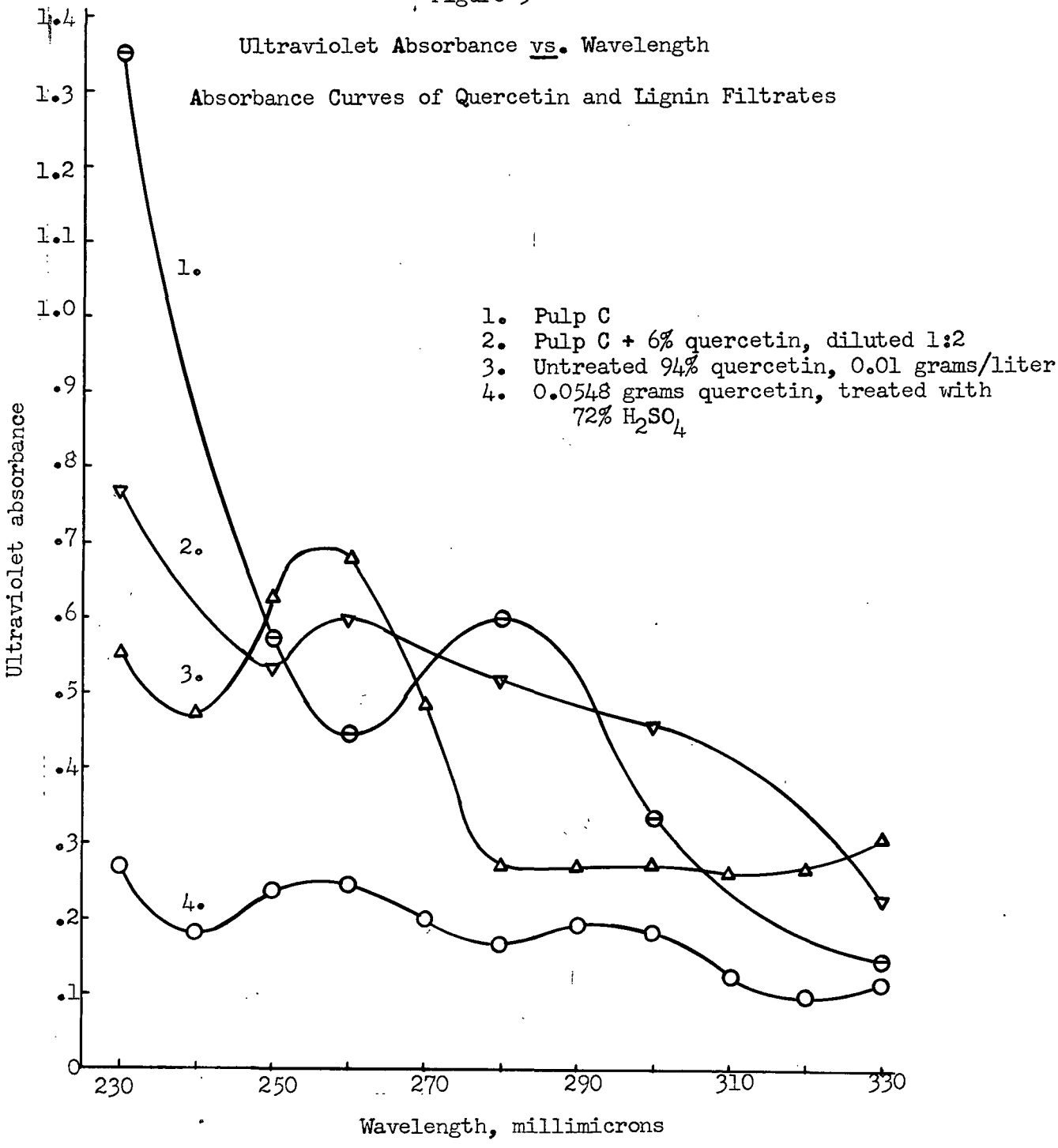
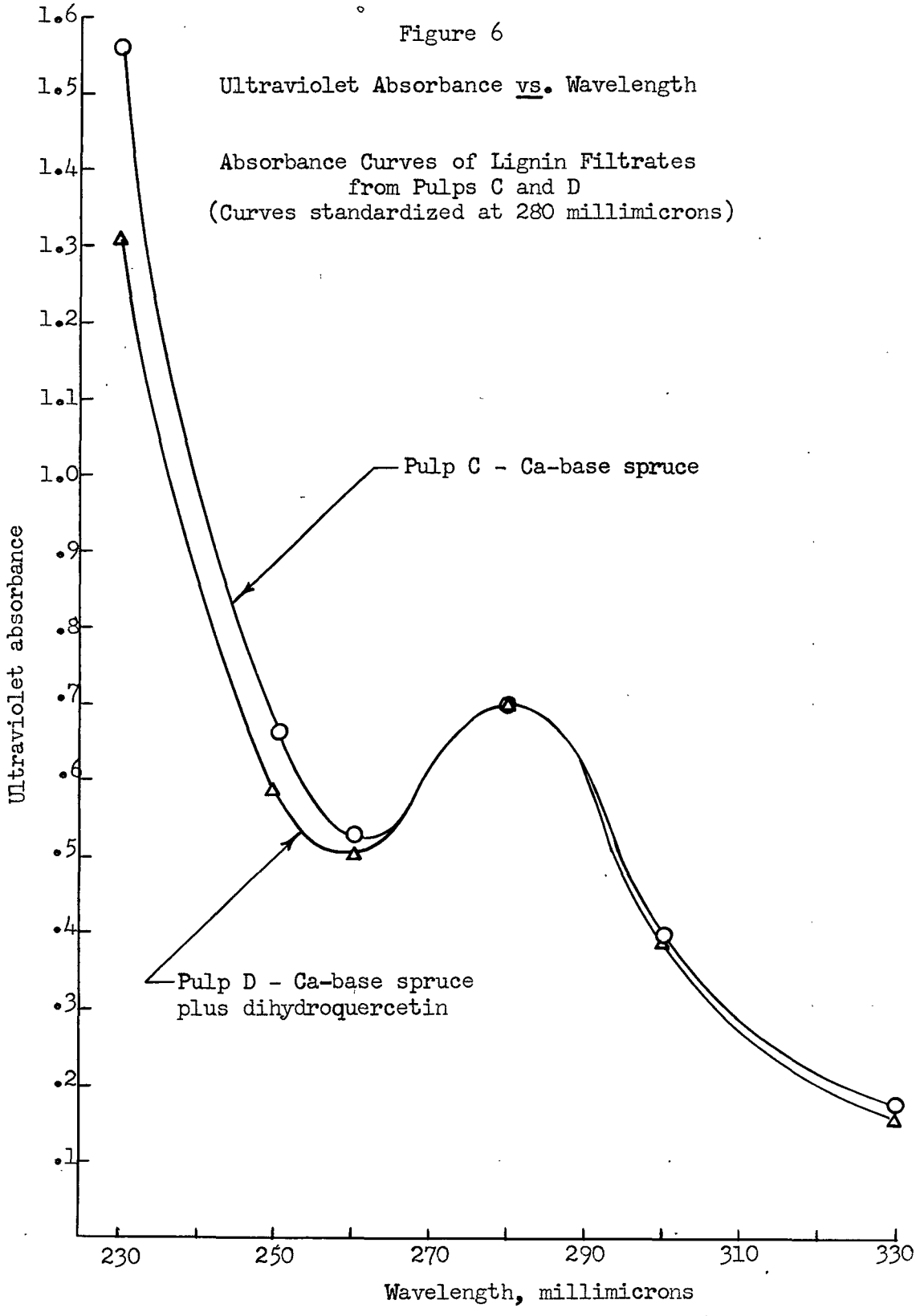


Figure 6

Ultraviolet Absorbance vs. Wavelength

Absorbance Curves of Lignin Filtrates
from Pulps C and D
(Curves standardized at 280 millimicrons)



THE DOUGLAS-FIR PULPING SERIES

THE EFFECT OF TEMPERATURE AND PRESSURE

Four sulfite cooks of Douglas-fir chips were conducted to study the effect of changing the maximum pulping temperature and to obtain data to explain the reported advantages of pulping Douglas-fir with soluble-base liquors. Calcium-base cooks were made with maximum temperatures of 130 and 140°C. Liquor samples were withdrawn during the progress of the cooks and were immediately analyzed for combined sulfur dioxide. The cooks were blown from maximum pressure 15 minutes after the liquor samples showed that the base had been completely consumed. These cooks were then repeated with sodium-base liquors, with the same total pulping times that had been used with the calcium base. The pulp analyses and the final liquor analyses from these cooks are presented in Table XIX.

The data of Table XIX show that the maximum cooking temperature had little effect on the lignin removal and in these calcium-base cooks, the higher temperatures appeared to be beneficial, particularly in regard to screenings. These results disagree with the findings of Chidester and McGovern (5) and Brookbank (7), who reported that decreased maximum temperatures tend to decrease the screenings in Douglas-fir pulps.

The high screenings in the calcium-base pulps could have been the result of the increased acidity which accompanied the complete exhaustion of the base. It is generally known that the insoluble lignosulfonates regain the ability to enter into a self-condensation if the conditions are sufficiently acidic to form the free lignosulfonic acids.

TABLE XIX

THE DOUGLAS-FIR PULPING SERIES

Douglas-fir pulping series cooking conditions

Cook	Ca-130	Na-130	Ca-140	Na-140
Maximum temperature, °C.	130	130	140	140
Cooking liquor base	Ca	Na	Ca	Na
Total cooking time, hr.	15-1/4	15-1/4	10-1/4	10-1/4
Final spent liquor[a]				
pH	0.92	1.52	0.90	1.31
Sulfate, mmol./l.	37.0	52.2	32.3	38.1
Thiosulfate, mmol./l.	21.0	19.5	27.1	22.2
Combined SO_2, %	-0.11	0.26	-0.06	0.38
Free SO_2, %	1.50	1.90	1.33	2.10
Pulp				
Total yield, %	51.4	51.0	47.7	51.0
Screened yield, %	40.3	50.8	43.6	50.0
Screenings, %	21.6	0.5	9.0	1.8
Permanganate number				
Total yield	28.3	21.6	29.9	26.3
Screened yield	24.2	--	25.8	25.7
Alcohol solubility, %	1.19	0.86	1.14	0.87
Insoluble lignin, %	5.7	2.0	4.8	3.0
Soluble lignin, %	1.9	3.2	1.4	3.5
Total lignin, %	7.6	5.2	6.2	6.5
Nonlignin yield, %	47.4	48.4	44.8	47.2
Lignin, % on ovendry wood	3.9	2.7	3.0	3.3

[a] The final liquor samples were obtained 15 minutes before the cooks were blown

Brookbank (7) and Chidester and McGovern (5) used a constant maximum pressure in their temperature comparisons. These investigators thereby decreased the free sulfur dioxide concentration in the cooking liquor by increasing the temperature of cooking. These pulping studies were conducted with the simultaneous changing of two variables—temperature and the sulfur dioxide concentration. Therefore, the improved pulping which was observed at the lower temperatures might have been primarily the result of increased sulfur dioxide concentration. However, these authors were partially justified in changing the two variables and reporting the results as a temperature effect, because in the common parlance of sulfite mills, a change in temperature is often assumed to take place with constant pressure.

In conjunction with their study of cooking temperatures, Chidester and McGovern (5) reported that changing the maximum pulping pressure, at constant temperature, had little effect on the pulping characteristics of Douglas-fir. This conclusion was based on the comparison of two calcium-base cooks with maximum temperatures of 145°C. The cooking liquor contained 7.0% total sulfur dioxide and 1.35% combined sulfur dioxide. The first cook was made with a maximum pressure of 75 p.s.i. and was continued for 9.5 hours. The second cook, with a maximum pressure of 150 p.s.i., was blown after 7.9 hours. The pulps were approximately the same and the conclusion was made that the maximum pressure had very little effect.

The data do not seem to justify the conclusion that pressure has little effect. The report did not explain the reasons for the differences between the cooking times, and no spent liquor analyses were

reported. It is improbable that both cooks were extended to the point of base depletion because of the large, 1.6-hour difference in cooking times. The increased sulfur dioxide concentration in the 150 p.s.i. cook probably would retard base depletion caused by sulfate formation—increased sulfur dioxide concentrations have been used commercially to delay bisulfite decomposition (28). If the high pressure had increased the amount of base consumed by the lignosulfonic acids, the pulp from this cook would have been more completely delignified. In conclusion, it would appear that the improved pulping of Douglas-fir which has been reported at reduced maximum temperatures might have been caused by an increased sulfur dioxide concentration in the digester.

The 130° cooks in the Douglas-fir pulping series had somewhat higher concentrations of sulfur dioxide than the cooks conducted at 140°C. Calculations, based on the data of Beazley, Campbell, and Maass (56) for the calcium oxide-water-sulfur dioxide system, showed that the 130°-75 p.s.i. cooks, at any given base content, had about 4 grams per liter more free sulfur dioxide than the 140°-85 p.s.i. cooks. This agrees very closely with the analyzed differences in free sulfur dioxide concentrations in the liquors from these cooks. (These liquor analyses are shown in Appendix A.) Therefore, the temperature changes in this series of Douglas-fir cooks were accompanied by changes in the sulfur dioxide concentration of the liquors, although the liquor changes were not as great as those which were present in the studies of other investigators who worked at constant pressure.

The intermediate liquor samples from the Douglas-fir cooks were studied chromatographically in an effort to observe changes involving dihydroquercetin. The temperature schedule for the 130° cooks, described previously, was 115° after 4 hours, 130° after 5 hours, and constant 130° for 10-1/4 hours. Positive tests for dihydroquercetin were observed in the 4-, 7-, and 9-hour liquor samples—this compound was difficult to detect in the later samples because of a darkened background on the chromatogram caused by other components of the liquors. Quercetin was present in small amounts in the 4-hour samples, and increased as the cooks were continued. These same trends were observed in the 10-1/4-hour, 140° cooks, where dihydroquercetin was present in the liquor after 7 hours of cooking. The presence of dihydroquercetin and quercetin in the liquor samples from the middle and latter portions of Douglas-fir cooks substantiates the earlier conclusions that these compounds do not act as strong phenolic inhibitors, which would have been quantitatively removed from the cooking liquor (19).

In summary, the pulping characteristics of Douglas-fir were studied at 130 and at 140°C.; the lower temperature cooks had slightly higher concentrations of sulfur dioxide in the digester. The maximum cooking temperature had little or no effect on the amount of lignin removed in Douglas-fir cooks which were extended to complete base exhaustion. The decreased screenings, which reportedly accompany reduced cooking temperatures (at constant pressure) in the calcium-base pulping of Douglas-fir, were not observed. However, the high screenings in the calcium-base cooks could have resulted from extending

these cooks beyond the point of base depletion. Chromatographic studies of liquor samples, taken at various times throughout these cooks, substantiated the previous conclusions that dihydroquercetin does not act as a strong phenolic inhibitor.

THE EFFECT OF COOKING LIQUOR BASE

It is generally known that all species of pulpwood show slightly improved sulfite pulping characteristics with the use of soluble-base cooking liquors. At a given total yield, the lignin in the pulp tends to be slightly lower than if calcium-base liquors are employed. However, Chidester and McGovern (8) reported that the sulfite pulping of Douglas-fir is greatly facilitated by the use of soluble-base acids. These results were obtained from a series of cooks in which longer cooking times were used with the soluble-base liquors.

The sulfite pulping characteristics of Douglas-fir with sodium- and calcium-base liquors are shown in Table XIX. With equal cooking times, the lignin contents and the permanganate numbers of the pulps are of the same order of magnitude, regardless of the type of cooking liquor. The major difference between the sodium- and calcium-base cooks was the pH and the available base in the final spent liquors. In both the calcium-base cooks, the available base was completely exhausted. The sodium-base cooks, in contrast, had 0.26% and 0.38% combined sulfur dioxide remaining in the final liquor. The lower base consumption with sodium-base liquors allows the use of longer cooking times before the base is completely consumed; the increased time of cooking then results in a more completely delignified pulp.

The difference between the base consumption in sodium- and calcium-base cooks is at least partially due to the sulfate which is formed in the bisulfite decomposition reactions. During the early portions of sulfite cooks, when bisulfite decomposition is relatively unimportant, the base is primarily consumed through the formation of salts of lignosulfonic acids, and the combined sulfur dioxide concentration, at any given time, is relatively independent of the type of base used. The sulfate formation, caused by bisulfite decomposition, becomes increasingly rapid toward the end of the cook and this is probably responsible for the large difference between the combined sulfur dioxide concentrations in sodium- and calcium-base cooks. The curves of dissolved sulfate and combined sulfur dioxide vs. cooking time for the Douglas-fir pulping series are shown in Figures 7 and 8. The data, upon which these curves are based, are presented in Appendix A.

The formation of sulfate in a calcium-base cook causes the base to be removed through the precipitation of calcium sulfate. In this case, two equivalents of calcium are required to neutralize one mole of sulfuric acid. In a sodium-base cook, the base reacts with sulfuric acid to form sodium sulfate, and eventually, sodium bisulfate. Richter (57) has shown that liquors of sodium bisulfate and sulfurous acid have almost the same effect in pulping as a solution of pure sulfurous acid; pulping is seriously hindered only when free sulfuric acid is present. In sodium-base cooks, only one equivalent of base is required to sufficiently neutralize one mole of sulfuric acid to prevent the acidity from becoming harmful. The reduced amount of base which is

Figure 7

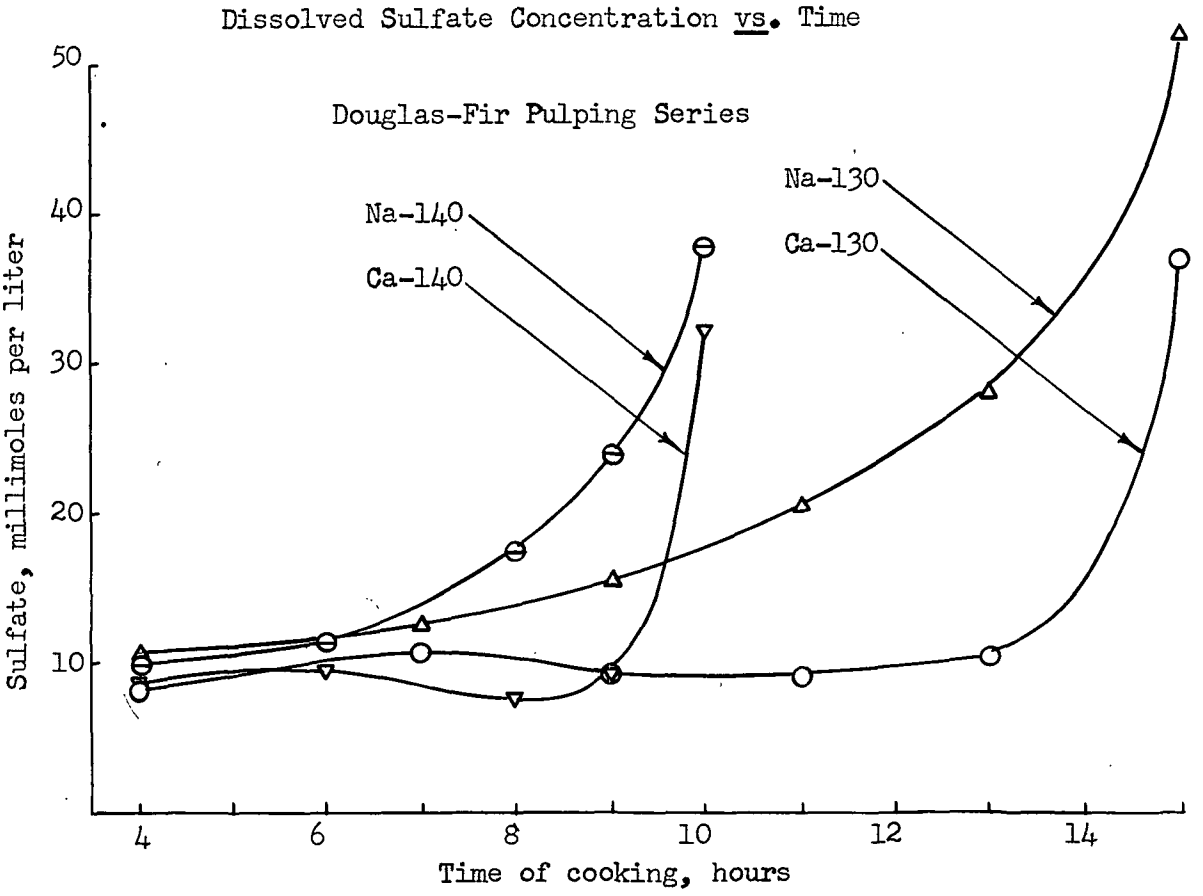
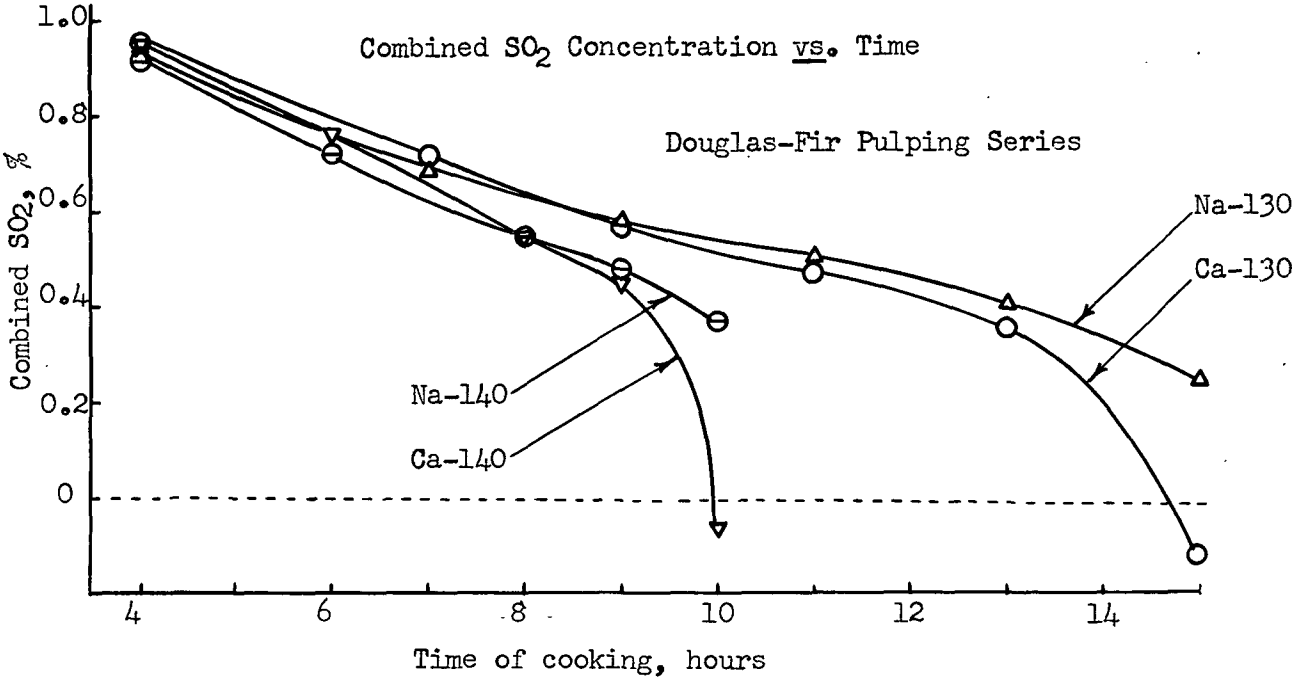


Figure 8



required to neutralize a given amount of sulfuric acid in sodium-base cooks causes sodium-base liquors to be advantageous in the sulfite pulping of any species of wood which requires extended cooking times.

THE EFFECT OF WOOD ON THE RATE OF BISULFITE DECOMPOSITION

The rates of thiosulfate increase in the sodium-base Douglas-fir cooks were compared with the previously reported data on thiosulfate increase in the absence of wood. A cooking liquor of 6.00% total sulfur dioxide and 1.40% combined sulfur dioxide was used to obtain the data in the absence of wood. The Douglas-fir cooks were made with 6.0% total sulfur dioxide and 1.25% combined sulfur dioxide. The curves of thiosulfate concentration vs. time at maximum temperature are shown in Figure 9.

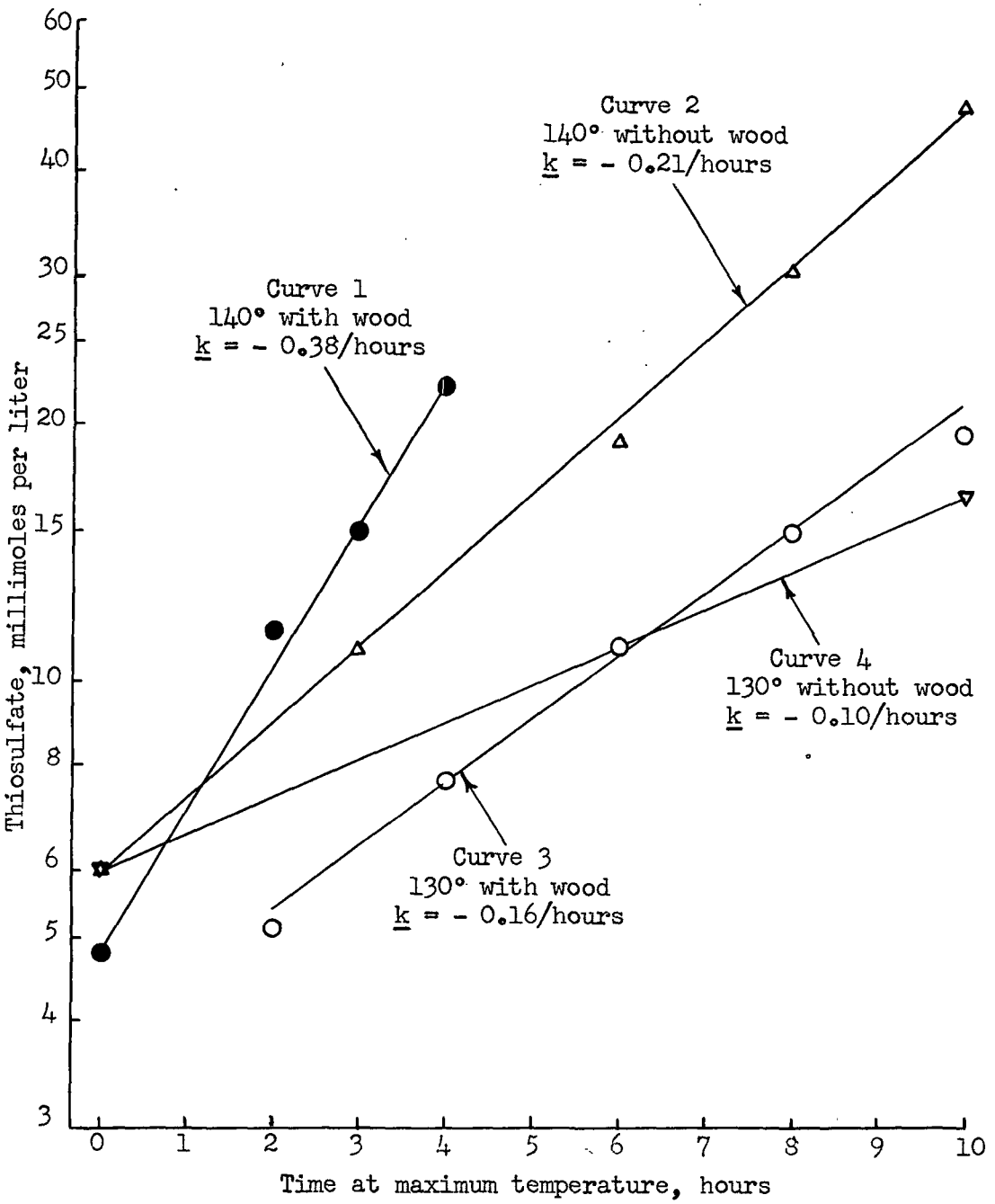
The data are sufficiently accurate for general comparisons of reaction rates, although the exact reaction rates shown in Figure 9 might be somewhat in error. Curve 3, obtained from the Douglas-fir Cook Na-130, does not accurately fit the straight line which was used to calculate the average specific reaction rate. Curve 4, with a maximum temperature of 130° in the absence of wood, is an estimated relationship which is based on only two experimental points. It was assumed that the 130° reaction, in the absence of wood, follows the straight-line relationship which was obtained at 140°C.

The curves of Figure 9 show that the rate of bisulfite decomposition appears to be accelerated by the presence of wood. The thiosulfate increase in sodium-base Douglas-fir cooks approximates a first-order

Figure 9

Log Thiosulfate Concentration vs. Time

Comparative Rates of Thiosulfate Increase



reaction with a rate of reaction greater than in the absence of wood. This increased rate of thiosulfate formation is probably due to one of two causes. The liquor changes which accompany the pulping reactions might cause the solution to become more favorable for bisulfite decomposition. Also, the formation of free sugars and their reaction with bisulfite, which would occur primarily in the middle and latter portions of the cooking cycle, might provide a source of thiosulfate that causes the total thiosulfate formation to follow the curve of a first-order reaction.

It is uncertain whether the presence of wood in a sulfite cook causes changes in the liquor decomposition that would result in accelerated bisulfite decomposition. During the course of a sulfite cook, both the sulfur dioxide concentration and the base concentration in the liquor are reduced. These would probably exert opposite effects on the rate of bisulfite decomposition. The over-all effect causes the cooking liquor to become more acidic and, according to Foerster (26), increased acidity decreases the rate of bisulfite decomposition. The relative rates of acidity increase, with and without the presence of wood, are not known.

The increased rate of bisulfite decomposition in the presence of wood is probably at least partially due to the formation of thiosulfate catalyst through the oxidation of sugars by bisulfite. However, the relative contribution of this effect cannot be determined from these data.

In conclusion, bisulfite decomposition seems to proceed more rapidly in the presence of wood than in the absence of wood. The small amount of data prevents the explanation of this effect.

GENERAL SUMMARY

The precipitate formed in the calcium-base sulfite cooks of Douglas-fir was found to be primarily anhydrous calcium sulfate. The precipitates were collected from three different cooks and analyzed by a procedure developed in the preliminary portion of this program. In each precipitate, the sulfate, calculated as anhydrous calcium sulfate, was about 90% of the total weight. Small amounts of free sulfur were also detected. These results indicated that the precipitate was the result of bisulfite decomposition.

Dihydroquercetin was extracted from Douglas-fir bark, and purified. The identity and purity of the final product was established by the melting point, the optical rotation, and chromatographic comparisons. A chromatographic system for the separation of dihydroquercetin from quercetin was developed.

A series of experiments in the absence of wood, showed that dihydroquercetin was dehydrogenated to quercetin and the bisulfite was reduced to thiosulfate. Quercetin yields were 45 to 50%. The thiosulfate promoted bisulfite decomposition in an autocatalytic, first-order reaction.

Phloroglucinol, resorcinol, and catechin had no effect on the stability of sulfite cooking liquor. The phloroglucinol and resorcinol were not changed by the sulfite cook. Catechin was partially converted to other unidentified compounds.

Formic acid, free sulfur, and free sugars form thiosulfate in sulfite cooking liquor. The sugars reacted with the bisulfite to form approximately 50% of the theoretical yield of thiosulfate. The theoretical amount of thiosulfate was formed in the reduction of bisulfite by formic acid.

The rate of bisulfite decomposition is strongly dependent on the temperature. Between 130 and 140°C. the speed of the reaction was doubled for each temperature increase of 5°C. The effect of temperature appeared to be even greater between 140 and 145°C.

Chromatographic study of wood extracts showed that the alcohol-benzene extraction removed practically all of the dihydroquercetin from Douglas-fir. (Previously published work had shown that the source of the pulping resistance of Douglas-fir could not be removed by alcohol-benzene extraction.) The spruce alcohol-benzene extract contained an unidentified compound which was moved by the 0.01 N hydrochloric acid developer and was colored by the spray reagent of ferric chloride and potassium ferricyanide. Separate tests showed that dihydroquercetin was present in both the sapwood and the heartwood of Douglas-fir.

Comparison of the pulping characteristics of untreated spruce chips with those from chips that had been impregnated with dihydroquercetin showed that this compound acted as a mild pulping inhibitor which slightly retarded, but did not prevent, the removal of the lignin. This showed that dihydroquercetin does not conform to Erdtman's theory of phenolic inhibitors. None of these cooks showed evidence of blocked

diffusion that might have been caused by the formation of a precipitate in the pores of the chips.

Although dihydroquercetin was a strong promoter of bisulfite decomposition in the absence of wood, it had little or no effect on these reactions in the sulfite cooks of spruce. The formation of quercetin in these cooks showed that the compound had been oxidized and presumably the bisulfite had been reduced to thiosulfate. Spruce cooks, with and without thiosulfate in the cooking liquor, showed that the presence of wood caused thiosulfate to be removed from the liquor during the first portion of the cooking cycle and thereby prevented it from catalyzing bisulfite decomposition.

Quercetin was formed in all the sulfite cooks that had originally contained dihydroquercetin. Quercetin, like dihydroquercetin, was found to be a weak pulping inhibitor. The pulps from the cooks containing these compounds were bright yellow when blown and, upon standing, they changed to a yellowish-tan or tan. Quercetin increased the permanganate number of these pulps and it might have increased the results of the lignin determinations.

Comparison of the pulping characteristics of Douglas-fir with those of spruce and spruce impregnated with dihydroquercetin showed that the rates of carbohydrate removal and bisulfite decomposition were approximately the same as with spruce. There was no evidence of blocked diffusion in the chips. Over half of the Douglas-fir lignin which remained after 9 hours of cooking was removed by extending the cook an

additional 1-1/2 hours—this showed that serious phenolization of the lignin had not occurred. The difficulty in the sulfite pulping of Douglas-fir is the slow rate of lignin removal; the lignin removal was much slower than with spruce impregnated with dihydroquercetin. The slow rate of lignin removal allowed the bisulfite decomposition, which proceeded at a normal rate, to reach dangerous proportions before the delignification was completed. The formation of sulfuric acid through bisulfite decomposition caused the cooking liquor base to be removed from the liquor by the precipitation of calcium sulfate.

Chromatograms of the intermediate liquor samples from Douglas-fir cooks showed that dihydroquercetin was present in liquors taken from the early and middle portions of the cooking cycles. The presence or absence of this compound in the final hours of the cooks could not be confirmed because other liquor compounds formed a dark background on the chromatograms. The quercetin content of the liquors increased throughout the cooks. These observations indicated that at least a portion of the dihydroquercetin had not combined with the lignin.

The sulfur contents of the lignin in Douglas-fir pulps were similar to those in spruce pulps. The sulfur content of the lignin was calculated from the sulfur in the pulp and the lignin in the pulp. This study was complicated by the undertain nature of the lignin analyses and accurate comparisons between the two species could not be made. The results showed that Douglas-fir lignin can be sulfonated to a sulfur content of over 6%— sulfur contents of this magnitude could not have been obtained if the lignin had reacted with a strong phenolic inhibitor.

The beneficial effects which reportedly accompany the use of reduced maximum temperatures in sulfite cooks of Douglas-fir were not observed. Comparisons of pulps from calcium- and sodium-base cooks showed that the base had practically no effect on the amount of lignin remaining in the pulp after a given time of cooking.

The calcium-base Douglas-fir cooks were continued to the total exhaustion of the base. The sodium-base cooks, with equal cooking times, had a considerable amount of available base in the final spent liquors. Also, the pH of the final sodium-base liquors was considerably higher than with calcium. The difference between the rates of base consumption appeared almost entirely in the final two hours of the cooks when the sulfate formation was rapid; the difference between the base consumption in calcium- and sodium-base cooks appeared to be dependent on the meachanism of sulfuric acid neutralization. The results showed that a major advantage of soluble-base cooking liquors is the result of reduced base consumption which allows the cooking time to be extended.

CONCLUSIONS

1. The major difficulty in the sulfite pulping of Douglas-fir is the retarded rate of lignin removal. The Douglas-fir lignin can be sulfonated and the pulping resistance is not the result of a lignin-inhibitor complex which cannot be removed by extending the time of cooking.

2. Although the Douglas-fir lignin is removed more slowly than spruce lignin, the rates of carbohydrate removal and bisulfite decomposition are approximately the same in sulfite cooks of these two species of wood.

3. The major portion of the resistance of Douglas-fir to sulfite pulping probably cannot be attributed to the presence of dihydroquercetin.

4. Dihydroquercetin is a mild pulping inhibitor. It slows the rate of lignin removal in a sulfite cook, but it does not form an insoluble lignin-inhibitor complex which cannot be removed by extending the time of cooking. Therefore, it does not conform to the present theory of phenolic inhibitors.

5. Dihydroquercetin reacts with bisulfite in the cooking liquor to form quercetin and thiosulfate. In the absence of wood, the thiosulfate promotes bisulfite decomposition in an autocatalytic, first-order reaction which forms sulfate and thiosulfate.

6. Dihydroquercetin, in concentrations of 17 millimoles per liter, has little or no effect on sulfite liquor stability in a conventional sulfite cook of spruce. The thiosulfate, formed in the early portion of the cook through the reaction between bisulfite and dihydroquercetin, is partially removed from the liquor by the wood or its reaction products, and is rendered unavailable for catalyzing bisulfite decomposition.

7. The precipitate formed in the calcium-base sulfite pulping of Douglas-fir is primarily anhydrous calcium sulfate. The sulfate is one of the end products of bisulfite decomposition. The slow rate of lignin removal in a Douglas-fir cook allows the bisulfite decomposition, which proceeds at a normal rate, to form large amounts of sulfate before the delignification reactions near completion. The precipitation of calcium sulfate removes the base from the solution. It is generally known that cooking in the absence of base causes serious damage to the pulp.

8. The primary advantage of sodium-base liquors over calcium-base liquors in the sulfite pulping of Douglas-fir is that less base is consumed in the sodium-base cooks. The lower base consumption allows longer cooking times and more complete delignification with a given amount of base.

LITERATURE CITED

1. Wells, Sidney D., and Rue, John D. The suitability of American woods for paper pulp. U.S. Dept. Agriculture Bull. No. 1485, Washington, U.S. Govt. Print. Off., 1927. 102 p.

2. Beuschlein, W. L., Paper Trade J. 88, no. 19:66-67(T.S. 147-148) (May 9, 1929).

3. Bailey, A. J., Paper Ind. 16:480-483(1934).

4. Brookbank, E. B., and Brauns, F. E., Paper Trade J. 110, no. 5: 33-35(T.S. 55-57)(Feb. 1, 1940).

5. Chidester, G. H., and McGovern, J. N., Paper Trade J. 110, no. 11: 39-42(T.S. 145-148)(March 7, 1940); Tech. Assoc. Papers 23:322-325 (1940).

6. Pew, John C. A flavanone from Douglas-fir heartwood. Forest Products Laboratory Report R1692. Madison, Wis., 1947. 17 p. Tappi 32, no. 1:39-41(1949).

7. Brookbank, E. B., Jr., Paper Trade J. 108, no. 7:30-38(T.S. 68-76) (Feb. 16, 1939); Tech. Assoc. Papers 22:556-564(1939).

8. Chidester, G. H., and McGovern, J. N., Paper Trade J. 113, no. 9: 34-38(T.S. 98-102)(Aug. 28, 1941); Tech. Assoc. Papers 24:226-230 (1941).

9. Hatch, R. S., and Holzer, W. F. Pacific coast pulpwoods. In TAPPI Monograph Series. No. 4. Especially p. 160. New York, Technical Association of the Pulp and Paper Industry, 1947.

10. McGovern, J. N., and Chidester, G. H., Paper Trade J. 111, no. 24: 35-38(T.S. 305-308)(Dec. 12, 1940); Tech. Assoc. Papers 24:579-582 (1941).

11. Gishler, P. E., and Maass, O., Can. J. Research 13B:370-379(1935).

12. Benson, Henry K., U.S. patent 1,805,799(May 19, 1931).

13. Harnist, G., German patent 469,342(1920); cited by (14).

14. Bryde, Ø., Norsk Skogind. 3:169-172(1949).

15. Bialkowsky, H. W. Personal communication, 1953.

15a. Kurth, E. F., and Chan, F. L., J. Am. Oil Chemists Soc. 28:433-436(1951).

16. Sen, Biswaneth. Action of sodium bisulfite on lignin model compounds. Doctor's Dissertation. Appleton, Wis., The Institute of Paper Chemistry, 1952. 68 p.

17. Kurth, E. F., Ind. Eng. Chem. 45:2096-2097(1953).

18. Migita, Nobuhiko, Nakano, Junzs, Sakai, Isamu, and Ishi, Shoichi, Japan Tech. Assoc. Pulp Paper Ind. 6:476-480(1952).

19. Erdtman, Holger, Svensk Papperstidn. 42:344-349(1939).

20. Erdtman, Holger, Tappi 32, no. 7:303-305(1949).

21. Erdtman, H., Cellulosechemie 18:83-92(1940).

22. Erdtman, Holger, Lindgren, Bengt O., and Pettersson, Tage, Acta. Chem. Scand. 4:228-238(1950).

23. Graham, J. S., British patent 5,365(1882); cited by (24).

24. Hagglund, Erik, and Hedborg, Fritz, Svensk Papperstidn. 38: 318-320(1935).

25. Adler, Erich, and Stockman, Lennart, Svensk Papperstidn. 54: 477-482(1951).

26. Foerster, F., Lange, F., Drossbach, D., and Seidel, W., Z. Anorg. allgem. Chem. 128:245-342(1923).

27. Klason, Peter, Wochbl. Papierfabr. 41:464-468, 541-547(1910).

28. Anderson, M. S., and McKnight, G. S., Jr., Tappi 36, no. 4:151-153 (1953).

29. Routala, O., and Pohjola, A., Finnish Paper and Timber J. 16: 289-290, 292-294, 296(1934).

30. Hagglund, Erik, Johnson, Torsten, and Urban, Helmut, Ber. 63B: 1387-1395(1930).

31. Hagglund, Erik, Tek. Tid. Uppl. C. Kemi 62:49-50, 60-64(1932). C.A. 26:6119(1932).

32. Hagglund, Erik, and Menzinski, Georg, Ber. 68B:822-824(1935).

33. Stockman, Lennart, Svensk Papperstidn. 54:621-627(1951).

34. Kurtenacker, Albin. Analytische Chemie der Sauerstoffsauren des Schwefels. Stuttgart, F. Enke, 1938. 216 p.

35. Samuelson, Olof, and Westlin, Arne, Svensk Papperstidn. 50, no. 11B: 149-154(1947).

36. Stam, Hellmuth, Seipold, Otto, and Goehring, Margot, A. Anorg. allgem. Chem. 247:277-306(1941); C.A. 37:2290.

37. Zil'berman, Ya. I., and Khmel'nitskaya, I. L., J. Applied Chem. (USSR) 14:486-491(1941); C.A. 36:2222.

38. Hergert, Herbert L., and Kurth, E. F., Tappi 35:59-66(1952).

39. Barton, G. M., Evans, R. S., and Gardner, J. A. F., Nature 170, no. 4319:249-250(1952).

40. Sander, A., Paper Trade J. 71, no. 10:50, 62(Sept. 2, 1920).

41. Sillen, Lars Gunnar, Svensk Papperstidn. 49:387-392(1946).

42. Samuelson, Olof, Svensk Papperstidn. 43:575-581(1946).

43. Browning, B. L., and Bublitz, L. O., Tappi 36, no. 10:452-458 (Oct., 1953).

44. Richtzenhain, Hermann, and Dryselius, Elisabeth, Svensk Papperstidn. 56:324-327(1953).

45. Lea, David Chester. The effect of the neutral sulfite semichemical cook on the hemicelluloses of aspenwood. Doctor's Dissertation. Appleton, Wis., The Institute of Paper Chemistry, 1953. 89 p.

46. Barton, John Selby. Reaction of lignin with acid sodium chlorite. Doctor's Dissertation. Appleton, Wis., The Institute of Paper Chemistry, 1948. 91 p.

47. Naghski, J., and Krewson, C. F., J. Am. Pharm. Assoc. 42:66-68(1953).

48. Mason, Frederick A., J. Soc. Chem. Ind. 47:269-276T(1928).

49. Campbell, W. G., and McDonald, I. R. C., J. Chem. Soc. 1952: 3180-3183.

50. Von Wacek, A., and Shroth, D., Holz Roh- u. Werkstoff 9:7-11 (1951).

51. Kurth, E. F., and Chan, Frank L., J. Am. Leather Chemists Assoc. 48:20-32(1953).

52. Sillen, Lars Gunnar, Svensk Papperstidn. 50:339-345(1947).

53. Aronosvky, S. I., and Gortner, Ross Aiken, Ind. Eng. Chem. 25: 1260-1265(1933).

54. Brauns, Friedrich Emil. The chemistry of lignin. New York, Academic Press, 1952. 808 p.

55. Brauns, F. E. The proven chemistry of lignin. In TAPPI Monograph Series. No. 6. Especially p. 122. New York, Technical Association of the Pulp and Paper Industry, 1947.

56. Beazley, Warren B., Campbell, W. Boyd, and Maass, O. The physical properties of sulphite liquors. Canada. Dept. of Mines and Resources. Lands, Parks and Forests Branch. Dominion Forest Service. Bulletin 93. Ottawa, J.O. Patenaude, 1938. 48 p.

57. Richter, George A., Tappi 36, no. 5:228-233(1953).

APPENDIX A

ADDITIONAL PULPING DATA

TABLE XX

SPRUCE PULPING SERIES LIQUOR ANALYSES

Cook I - No additives [a]

Hour	Millimoles per liter Sulfate	Thiosulfate	pH	Free SO_2, %	Combined SO_2, %
0	15.7	0.4	1.50	6.00	1.25
3	23.4	1.2	1.61	3.94	0.91
5	24.3	2.5	1.49	3.43	0.69
7	28.0	7.2	1.46	2.58	0.51
9	46.1	17.5	1.32	2.02	0.27
10	83.5	23.9	1.13	1.44	0.01

Cook II - Liquor containing 7 millimoles per liter thiosulfate

Hour	Millimoles per liter Sulfate	Thiosulfate	pH	Free SO_2, %	Combined SO_2, %
0	3.5	7.0	1.59	6.00	1.25
3	15.8	5.1	1.67	3.98	0.99
5	19.6	4.6	1.57	3.42	0.67
7	25.3	9.4	1.49	2.66	0.50
9	44.0	18.7	1.40	2.11	0.31
10	81.1	30.6	1.16	1.52	0.10

[a] This cook was conducted with liquor that was 3 days old and was restandardized immediately before using.

TABLE XXI

COMPLETE MIXED PULPING SERIES DATA

Mixed pulping series cooking conditions

Cook	A	B	C	D	E	F
Wood pulped	Spruce	Spruce	Spruce	Spruce	D.-Fir	D.-Fir
Additive	None[a]	3.4% DHQ	None[a]	3.2% DHQ	None	None
Cooking liquor base	Na	Na	Ca	Ca	Ca	Ca
Total cooking time, hr.	9	9	9	9	9	10½
Drained liquor						
pH	1.53	1.49	1.40	1.38	1.38	1.39
Sulfate, mmol./l.	28.8	25.9	8.9	10.2	10.3	35.9
Thiosulfate, mmol./l.	15.0	19.4	14.3	18.2	16.8	14.8
Combined SO_2, %	0.56	0.63	0.47	0.47	0.46	-0.07
Free SO_2, %	2.72	2.64	1.93	2.23	2.46	1.38
Expressed liquor						
pH	4.00	3.92	3.70	3.67	4.35	1.73
Sulfate, mmol./l.	33.6	30.8	27.9	31.2	25.4	49.5
Thiosulfate, mmol./l.	18.0	21.6	18.4	22.8	22.0	12.9
Combined SO_2, %	0.42	0.50	0.39	0.39	0.43	-0.09
Pulp						
Total yield, %	49.9	51.1	50.1	50.5	59.0	50.1
Permanganate number	15.0	26.6	17.7	40.9	>45	38.0
Alcohol solubility, %	1.75	1.73	1.55	1.51	0.78	1.11
Insoluble lignin, %	1.2	4.1	2.2	7.0	14.8	8.3
Soluble lignin, %	3.6	3.0	3.1	2.6	3.2	2.2
Total lignin, %	4.8	7.1	5.3	9.6	18.0	10.5
Nonlignin yield, %	47.5	47.5	47.5	45.6	48.3	44.9
Lignin, % on ovendry wood	2.4	3.6	2.7	4.8	10.6	5.3
Sulfur, % in pulp	—	—	—	—	0.988	0.695
Sulfur, % on total lignin	—	—	—	—	5.5	6.6
Sulfur, % on insol. lignin	—	—	—	—	6.7	8.4

[a] Chips were given impregnation treatment with water alone.

TABLE XXI (Continued)

COMPLETE MIXED PULPING SERIES DATA

Mixed pulping series cooking conditions

Cook	G	H	I	J	K	L
Wood pulped	Spruce	D.-Fir	Spruce	Spruce	Spruce	Spruce
Additive	None	Water Extr.[b]	3.3%[c] DHQ	None	None	2.1% Quercetin
Cooking liquor base	Ca	Ca	Ca	Ca	Ca	Ca
Total cooking time, hr.	$10\frac{1}{2}$	$10\frac{1}{2}$	$10\frac{1}{2}$	$6\frac{1}{2}$	$7\frac{1}{2}$	9
Drained liquor						
pH	1.19	1.30	1.19	1.63	1.52	1.48
Sulfate, mmol./l.	33.5	30.0	44.4	9.5	9.1	10.1
Thiosulfate mmol./l.	28.4	19.7	25.6	7.1	10.9	20.5
Combined SO_2, %	-0.09	0.04	-0.17	0.66	0.55	0.44
Free SO_2, %	1.40	1.66	1.01	2.42	2.36	2.07
Expressed liquor						
pH	1.51	1.53	--	--	--	--
Sulfate, mmol./l.	48.3	37.0	--	--	--	--
Thiosulfate, mmol./l.	21.8	12.4	--	--	--	--
Combined SO_2, %	-0.05	-0.08	--	--	--	--
Pulp						
Total yield, %	44.0	49.4	46.1	65.7	57.2	51.4
Permanganate number	5.2	37.2	14.8	>45	32.5	36.2
Alcohol solubility, %	0.89	0.84	1.09	1.34	1.09	1.04
Insoluble lignin, %	0.3	7.2	1.8	13.1	6.3	4.3
Soluble, lignin, %	1.0	3.7	1.6	6.9	5.4	3.0
Total lignin, %	1.3	10.9	3.4	20.0	11.7	7.3
Nonlignin yield, %	43.4	44.1	44.6	52.5	50.5	47.6
Lignin, % on ovendry wood	0.6	5.4	1.6	13.1	6.8	3.8
Sulfur, % in pulp	--	--	--	0.924	0.579	--
Sulfur, % on total lignin	--	--	--	4.6	4.9	--
Sulfur, % on insol. lignin	--	--	--	7.1	9.2	--

[b] The chips were soaked in water at 70°C. for 60 hours with four changes of water. The extraction removed 2.9% of the original wood but the efficiency of dihydroquercetin removal was not determined.

[c] Chips were impregnated with 3.0% dihydroquercetin—the remainder was added to the cooking liquor.

TABLE XXII

DOUGLAS-FIR PULPING SERIES LIQUOR ANALYSES

Cook: Ca-130 Time to blow: 15-1/4 hours

Hour	Millimoles per liter Sulfate	Thiosulfate	pH	Free SO_2, %	Combined SO_2, %
0	2.7	0.3	1.52	6.00	1.25
4	8.2	1.8	1.60	4.11	0.95
7	10.8	5.6	1.68	2.92	0.73
9	9.4	8.7	1.52	2.72	0.57
11	9.1	11.6	1.47	2.52	0.48
13	10.4	18.2	1.32	2.24	0.37
15	37.0	21.0	0.92	1.50	-0.11

Cook: Na-130 Time to blow: 15-1/4 hours

Hour	Millimoles per liter Sulfate	Thiosulfate	pH	Free SO_2, %	Combined SO_2, %
0	4.5	1.2	—	6.00	1.25
4	10.6	1.9	1.66	3.97	0.93
7	12.5	5.1	1.73	3.18	0.69
9	15.4	7.7	1.68	2.90	0.59
11	20.6	11.0	1.68	2.64	0.51
13	28.0	15.0	1.62	2.47	0.42
15	52.2	19.5	1.52	1.90	0.26

Cook: Ca-140 Time to blow: 10-1/4 hours

Hour	Millimoles per liter Sulfate	Thiosulfate	pH	Free SO_2, %	Combined SO_2, %
0	3.6	0.3	1.53	6.00	1.25
4	8.6	1.2	1.55	4.28	0.96
6	9.6	5.9	1.50	3.22	0.78
8	7.9	14.4	1.43	2.32	0.56
9	9.3	21.3	1.28	2.07	0.45
10	32.3	27.1	0.90	1.33	-0.06

Cook: Na-140 Time to blow: 10-1/4 hours

Hour	Millimoles per liter Sulfate	Thiosulfate	pH	Free SO_2, %	Combined SO_2, %
0	4.4	0.4	1.59	6.00	1.25
4	10.0	1.8	1.63	4.00	0.93
6	11.4	4.8	1.70	3.11	0.73
8	17.4	11.5	1.47	2.48	0.57
9	24.0	15.0	1.40	2.29	0.49
10	38.1	22.2	1.31	2.10	0.38

TABLE XXIII

SOLUBLE LIGNIN CALCULATED AT DIFFERENT WAVELENGTHS

Wavelength, mmu.	230	250	280	300
Lignin absorptivity [a]	46.5	18.0	18.0	8.2
Soluble lignin, %				
Pulp A	3.6	4.1	4.4	5.6
B	3.0	3.3	3.9	4.9
C	3.1	3.3	3.7	4.2
D	2.6	3.0	3.5	4.7
E	3.2	3.6	3.8	5.0
F	2.2	2.5	3.2	4.3
G	1.0	1.3	2.1	2.7
H	3.7	4.7	5.8	7.3
I	1.6	2.2	3.5	4.5
J	6.9	8.6	7.8	10.5
K	5.4	6.4	6.4	8.2
L	3.0	3.8	6.8	5.7
Ca-130	1.9	2.5	3.8	5.0
Na-130	3.2	4.2	5.0	7.1
Ca-140	1.4	2.1	3.2	4.3
Na-140	3.5	4.7	5.2	7.5

[a] The absorptivity of spruce native lignin reported by Barton (46).

APPENDIX B

SPECIAL METHODS OF ANALYSIS

PROCEDURE FOR ANALYSIS OF MIXTURES OF SULFITE, THIOSULFATE, AND POLYTHIONATES

Starting material: Fresh or partially decomposed sulfite cooking acid

Determination of Iodine Consumption (A)

1. Pipet 10 ml. of the liquor into a 250 ml. Erlenmeyer flask containing about 75 ml. of water. Add several drops of phenolphthalein indicator and neutralize with 10% sodium hydroxide. Allow the mixture to stand for about 5 minutes.

2. Add 10 ml. of 10% acetic acid and starch indicator.

3. Oxidize with iodine to the starch endpoint. The milliequivalents of iodine consumed in this titration multiplied by 100 equals the value (A), expressed as milliequivalents per liter.

Determination of Iodine Consumption (B)

1. Pipet 100 ml. of the liquor into a 500 ml. Erlenmeyer flask containing about 150 ml. of water. Neutralize to the phenolphthalein endpoint and add 5 ml. of 10% sodium hydroxide in excess.

2. Allow the mixture to stand for about 5 minutes. Filter off any precipitate which may be formed.

3. Add 10% acetic acid to the phenolphthalein endpoint and add 10 ml. of 40% formaldehyde. Allow to stand for several minutes.

4. Again add 10% acetic acid to the phenolphthalein endpoint and acidify with an additional 25 ml. of 10% acetic acid.

5. Add starch indicator and determine the iodine consumption using a microburet or a 10 ml. buret. The starch endpoint can be greatly stabilized by the addition of 3 ml. of 1:1 hydrochloric acid just before the endpoint is reached. The number of milliequivalents of iodine multiplied by ten equals (B), expressed as milliequivalents of iodine per liter.

Determination of Iodine Consumption (C)

1. The ideal sample size for this step is determined from the volume of iodine solution used in the titration in the determination of (A). If the iodine consumption of 10 ml. of the liquor is less than 100 ml., a 10 ml. sample can be used in this step. If a greater volume of iodine is required, the sample size should be correspondingly reduced.

2. Pipet the sample into a 200 ml. volumetric flask containing 20 ml. of water. Add several drops of phenolphthalein and neutralize with 10% sodium hydroxide. Allow to stand for several minutes.

3. Add 5 ml. of 10% acetic acid, starch indicator, and iodine to the starch endpoint.

4. Remove the blue color with a drop of 0.4 N sodium sulfide solution.

5. Add 10% sodium hydroxide to the phenolphthalein endpoint.

6. Add exactly 10 ml. of freshly prepared 0.4 N sodium sulfide solution.

7. Begin to pass a stream of nitrogen gas into the flask. Do not allow the nitrogen to bubble through the solution.

8. Heat the flask to boiling and continue to hold near the boiling temperature for 10 minutes.

9. Cool the flask under a stream of cold water.

10. Prepare 30 ml. of zinc carbonate slurry by stirring in the dropwise addition of 15 ml. of 0.8 M zinc nitrate to 15 ml. of 10% sodium carbonate.

11. Stop the stream of nitrogen into the flask.

12. Slowly add the zinc carbonate slurry to the flask with intermittent shaking.

13. Dilute to the mark.

14. Filter the contents of the flask through a dry filter paper—vacuum filtration is undesirable.

15. Pipet out 100 ml. of the filtrate for titration.

16. Add starch indicator and 5 ml. of 10% acetic acid.

17. Determine the iodine consumption, using a microburet or a 10 ml. buret. Record the amount of iodine consumed.

18. Add about 50 ml. of distilled water to a clean 200 ml. volumetric flask. Add several drops of phenolphthalein and repeat steps 5 to 17 to obtain a blank determination on the sulfide solution.

19. Subtract the iodine consumption in step 18 from the iodine consumption in step 17. The net milliequivalents of iodine, corrected for the sample size, is the value (C), expressed in milliequivalents of iodine per liter of sulfite liquor.

Calculation of Results

Solve the equations:

$$2X + Y - Z = (A)$$

$$Y + Z = (B)$$

$$Y + 3Z = (C)$$

where:

X is the number of millimoles of sulfite per liter
Y is the number of millimoles of thiosulfate per liter
Z is the number of millimoles of tetrathionate per liter.

PROCEDURE FOR ANALYSIS OF DISSOLVED SULFATE IN THE PRESENT OF SULFITE, THIOSULFATE, AND POLYTHIONATES

Starting material: Partially decomposed sulfite cooking acid

1. Pipet 50 ml. of the liquor into a 250 ml. Erlenmeyer flask containing 10 ml. of 40% formaldehyde.

2. Add several drops of phenolphthalein and neutralize with 10% sodium hydroxide. Allow the solution to stand for several minutes.

3. Add several drops of starch indicator and 2 ml. of 1:1 hydrochloric acid.

4. Add iodine solution to the starch endpoint and remove the blue color with a drop of 0.1 N thiosulfate solution.

5. Transfer to a large beaker and dilute to 400 ml. Add 40 ml. of 0.1 N barium chloride solution dropwise while stirring the solution.

6. Allow the precipitate to settle for about an hour and filter through a weighed Gooch crucible with an asbestos filter pad. Wash the precipitate thoroughly.

7. Hold the crucible at a dull red heat in a muffle furnace for one hour.

8. Cool in a desiccator and weigh. Determine the net weight of the barium sulfate precipitate.

Calculation of Results

The weight of barium sulfate divided by 0.2334 equals the millimoles of sulfate in the original 50 ml. sample.

ANALYTICAL PROCEDURE FOR SOLID MIXTURES OF CALCIUM SULFATE, CALCIUM SULFITE, AND FREE SULFUR

Starting material: An accurately weighed sample of 0.2 to 0.5 grams of finely divided solid in a 250 ml. Erlenmeyer flask.

1. Add about 75 ml. of water, 10 ml. of 10% acetic acid, and 3 ml. of 1:1 hydrochloric acid.

2. Add starch indicator and immediately titrate with iodine to the starch endpoint. The milliequivalents of iodine consumed equals the value (A).

3. Add 5 ml. of 1:1 hydrochloric acid and allow the mixture to stand about 10 minutes with periodic stirring to dissolve the calcium sulfate.

4. Filter through a medium speed filter paper. Wash the precipitate with 1:10 hydrochloric acid and water. Allow the filtrate and washings to drain into an 800 ml. beaker.

5. Transfer the filter paper containing the free sulfur to a 250 ml. Erlenmeyer flask and add 100 ml. of 0.4 N sodium sulfite. Heat this mixture and hold it near the boiling point. Break up the filter paper.

6. The filtrate from step 4 is diluted to about 350 ml. and heated to a rolling boil. A solution of 0.1 N barium chloride is added dropwise with stirring. Add a minimum of 70 ml. of barium chloride solution for each half gram of sample.

7. Allow the barium sulfate to settle for an hour or more and filter through a weighed Gooch crucible containing an asbestos fiber filter mat. Wash the precipitate thoroughly with water. Discard the filtrate and washings.

8. Heat the crucible to a dull red color in a muffle furnace for one hour. Cool and weigh. The net weight of the precipitate divided by 0.2334 is the value (B).

9. The mixture from step 5 is allowed to boil for a half hour after the last visible traces of sulfur have dissolved. Water may be added from time to time to keep the liquid level fairly constant.

10. Cool the solution and add 10 ml. of 40% formaldehyde. Allow to stand for three to five minutes.

11. Filter out the disintegrated filter paper using a vacuum filtration. Wash the pulp mat with water.

12. Remove the pulp mat from the funnel and reslurry it in 100 ml. of water containing 10 ml. of 10% acetic acid. Repeat the filtration and the washing of the previous step.

13. Add several drops of phenolphthalein indicator solution to the combined filtrates and washings. Add 10% acetic acid to the phenolphthalein endpoint and then add 10 ml. more.

14. Immediately add starch indicator and titrate with iodine solution. Just before the starch-iodine endpoint is reached add 3 ml. of 1:1 hydrochloric acid. This tends to stabilize the endpoint. The milliequivalents of iodine consumed equals the value (C).

Calculation of Results

Millimoles of calcium sulfite = 1/2(A)

Millimoles of calcium sulfate = (B) - 1/2(A)

Milliatoms of free sulfur = (C)